— G.W. NELSON. —

PHYSICAL AND CHEMICAL EXAMINATION OF PAINTS, VARNISHES, AND COLORS

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DEDICATION.

To those engaged in the production or application of paint and varnish materials, and especially to those workers in the hundred laboratories that have been installed throughout the American paint industry since the inauguration of the Educational Bureau; whose combined labors are reflected, through surface protection, by the annual conservation of millions of dollars' worth of structural materials, by the vast improvement in industrial lighting, by the elimination of insanitary conditions, and by the production of pleasing and harmonious color effects in communities; this volume is dedicated.

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PREFACE

The absolute futility of analysis as a basis of varnish evaluation is pointed out on page 125. The character and suitability of varnishes can only be judged from physical tests. The properties of many pigments and oils are learned through similar means, and in this manner information may be gleaned that is often far more useful than that afforded by chemical analysis. In a similar manner, physical tests of paint are rapidly being developed that may ultimately make it possible to predict the serviceability of various products. In this volume, therefore, an attempt has been made to outline or at least refer to the more important physical tests that every paint and varnish laboratory should be familiar with. Physical tests previously published in Scientific Section Circulars have also been abstracted for presentation.

The book entitled "Analysis of Paints" and a chapter on the same subject, prepared by the writer and J. A. Schaffer for Scott's "Standard Methods of Chemical Analysis" (two volumes, 1922) contained methods that have been used to a considerable extent in the paint and varnish industry. Some of the material referred to has been abstracted for presentation herein, through the permission of D. Van Nostrand Co., New York. The more important methods adopted by the American Society for Testing Materials (see reports of Committee D-1, A. S. T. M., 1916–1922), as well as several methods privately communicated, are also contained in the present volume. A large amount of important material heretofore unpublished is also added. This includes methods for the analysis of organic red colors; bituminous enamels, varnishes and cements; analysis of mixed driers; physical and chemical assay of colors; optical examination of white pigments with tables giving their spectral composition and relative hiding power, etc.

Due to the great dissimilarity of specifications for paints and varnishes previously used by the various departments of the United States Government, a member of the War Service Committee of the Paint Industry suggested early in 1918 that steps be taken to inaugurate a plan for correlating all the specifications of the various departments into a series of specifications that would be acceptable to all. This idea undoubtedly led to the formation of the U. S. Interdepartmental Committee on Paint Specification Standardization, of which the writer is a member, whose labors have resulted in specifications, which have been bound into this volume.

To the following the writer is indebted for material or suggestions in the preparation of this book: P. H. Walker, L. L. Steele, F. W. Smither, E. F. Hickson, and E. H. Berger, all of the Bureau of Standards; J. A. Schaeffer, A. H. Pfund, L. E. Barton, F. G. Breyer, P. R. Croll, A. F. Brown, P. H. Butler, R. E. Coleman, P. C. Holdt, and other associates.

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CHAPTER I.

PHYSICAL EXAMINATION OF PAINT MATERIALS

There is given below a series of physical methods by which the character of various pigments, colors, oils and similar products may be judged. For the chemist who desires to become familiar with the work of other investigators of the physical properties of these materials, the following references are given. Abstracts of some of these articles are, however, included in this volume.

Optical Properties and Theory of Color of Pigments and Paints—H. E. Merwin. Proc. Amer. Soc. Test. Mater. XVII—Part II, 494.

Determination of Absolute Viscosity by the Saybolt Universal and Engler Viscosimeters—Winslow H. Herschel. *Ibid.*, 551.

The Standard Saybolt Universal Viscosimeter—Winslow H. Herschel. *Ibid.*, XVIII—Part II, 363.

The Variable Pressure Method for the Measurement of Viscosity—E. C. Bingham. *Ibid.*, 373.

Paint, a Plastic Material and not a Viscous Liquid: the Measurement of its Mobility and Yield Value—E. C. Bingham and Henry Green. *Ibid.*, XIX—Part II, 640.

An Instrument for Measuring the Hiding Power of Paints—R. L. Hallett. *Ibid.*, XX—Part II, 426.

A New Colorimeter for White Pigments and Some Results Obtained by Its Use—A. H. Pfund. *Ibid.*, 440.

Further Development of the Plastometer and its Practical Application to Research and Routine Problems—H. Green. *Ibid.*, 451.

Stress-Strain Measurements on Films of Drying Oils, Paints and Varnishes—H. A. Nelson. *Ibid.*, XXI, 1111.

The Use of Secondary Reference Standards in Process Problems of Color Measurement—H. S. Busby. *Ibid.*, 1139.

Relation of Yield Value and Mobility of Paints to Their so-called Painting Consistency—J. E. Booge, E. C. Bingham, and H. D. Bruce. *Ibid.*, XXII.

Some Physical Properties of Paints—P. H. Walker and J. G. Thompson. *Ibid.*, XXII.

Accelerated Weathering of Paints on Wood and Metal Surfaces—Harley A. Nelson. *Ibid.*, XXII.

An Analysis and Comparison of Systems of Color Measurement and Some Notes on Interchangeability in Color Measurement—H. S. Busby. *Ibid.*, XXII.

An Application of the Pfund Colorimeter to the Determination of Tinting Strength—J. A. Calbeck. *Ibid.*, XXII.

Hiding Power of Paints—R. L. Hallett. *Ibid., XXII.*

Laboratory methods for determining the physical properties of paint and varnish films are very much to be desired. The field is of great importance on account of the growing tendency of specification writers to set requirements for varnishes almost wholly on physical properties, allowing the varnish maker to use whatever material he finds best suited to produce products that will meet the requirements. Certain physical properties, how-

ever, are difficult to define. For instance, requirements for such characteristics as hardness, elasticity, and gloss should be made definite, so that the manufacturer may check up his products as closely as he might by a chemical analysis of an oil paint. The field opened up by such work is a wide one, and so far but little explored. Excellent work, however, has been done during the last few years by Breyer, Pfund, Bingham, Green and Hallett, and it is understood that these investigators are now making further progress along similar lines.*

In 1908 probably one of the first efforts to devise and definitely define physical tests on paint films was made in the old laboratories of the Scientific Section and published in the First Annual Report of the Section (1908). In this report, methods of preparing paint films were outlined and apparatus for determining the tensile strength (Perry filmometer), as well as methods for determining opacity, permeability, effect of weathering, etc., were described. Difficulty was had, however, in some cases with the preparation of films of suitable size and in preserving them for experimentation. While open to criticism from many angles, this early work was productive of much information.

With a view to resuming this work and of making a further study of the possibilities along this line, the writer has recently completed a series of tests which indicate that suitable films may be made on a standardized form of bond paper and tested with much less difficulty than when formed on gelatinized or mercurized metal and stripped therefrom, as in the early experiments.

In the new tests a series of paints and varnishes were applied in two coat work to a bond paper showing a fairly constant Mullen bursting test. After drying, a series of the painted sheets were tested for thickness, bursting strength, and tensile strength, with a direct reading spring micrometer, Mullen tester, and Scott apparatus, respectively. Duplicate sections about 18″ square of the coated paper were then lightly fastened at the ends to wooden decks, and exposed on the laboratory roof, facing south, at an angle of 45 degrees to the vertical. At the end of two months, the specimens were retested. The results are recorded in the charts.

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* Hiding Power of White Pigments and Paints.

A. F. Pfund—Jour. Franklin Inst., 1919. The Colorimetry of Nearly White Surfaces.

A. F. Pfund—Jour. Franklin Inst., 1920. An Instrument for Measuring the Hiding Power of Paints.

R. L. Hallett, Proc. A. S. T. M., 1920. A New Colorimeter.

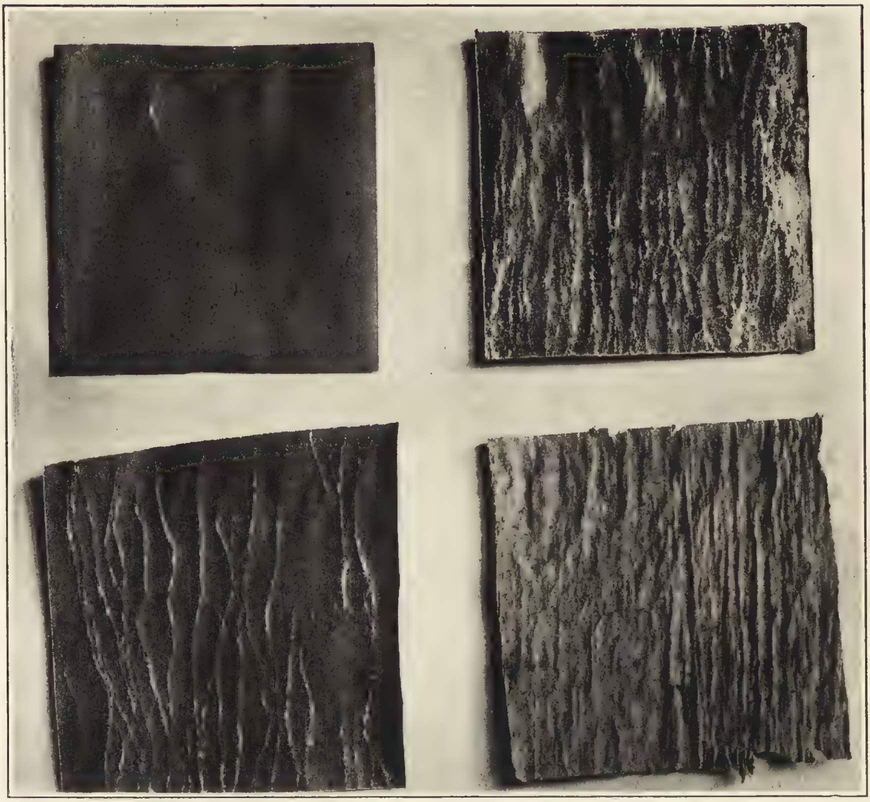

FIG. 1
Samples After Exposure on Paper
Top—Long Oil Spar
Lower—High Gum Rubbing
Top—High Gum
Lower—A Cellulose Dope

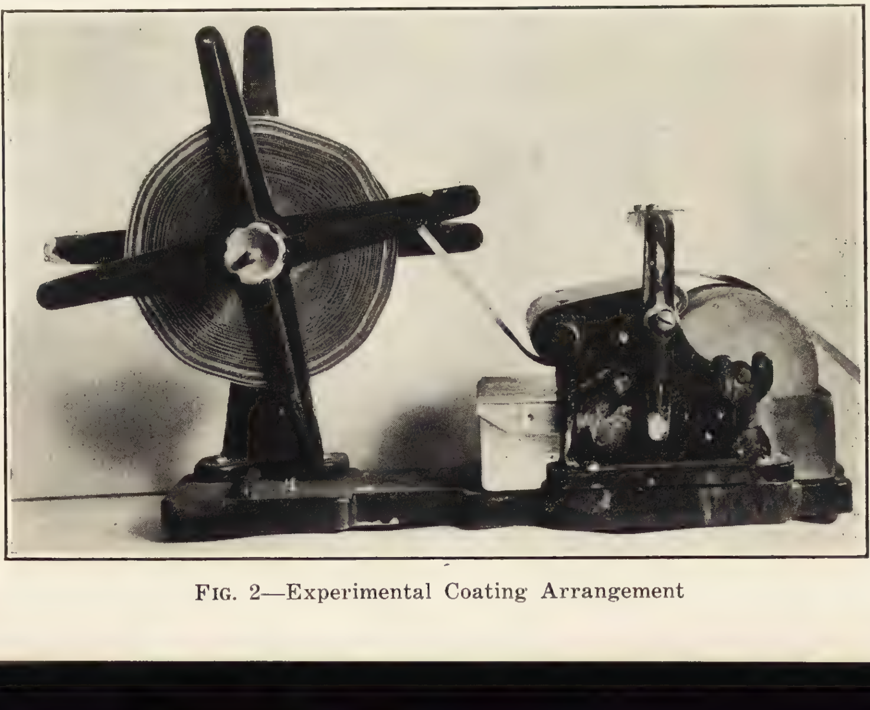

FIG. 2—Experimental Coating Arrangement

When first approaching the problem, it was thought advisable, if possible, to devise an apparatus that would apply a coating of uniform thickness of any kind of paint product to be tested. Much experimental work was carried out, and several marketed gummed-paper wrapping tape machines were experimented with. The results, however, due to difficulties in exerting uniform tension upon the rolled paper, were not encouraging. Apparatus with steel and with glass coating blades, similar to those used in the mechanical coating of oilcloth with white enamel, was also constructed and experimented with, but ultimately found to be mechanically deficient. On full size apparatus in oil cloth factories, paper was coated with films of practically uniform thickness, but such a machine would not be applicable to or available for routine testing work. Pending the development of a mechanically perfect coating machine for laboratory use, the writer resorted to the old-fashioned hand-brush method of paint application. It appears, as shown by the several measurements in the charts, that most films applied by this method do not vary in thickness to any marked extent at various sections on one coated sheet.

It was noted on the day following the drying of the last coat of paint or varnish that the paper sheets coated with interior short oil varnish would upon even slight bending, show a large number of cracks and checks, while all long oil varnish products were very flexible. In fact, much information regarding the physical nature of the various coatings was obtainable by handling the coated sheets.

When coating the specimens, it was noted that some of the liquids, such as raw linseed oil and raw linseed oil paints, rapidly penetrate the paper and thus waterproof the back as well as the front. Other coatings, such as rapid drying varnishes or heavy bodied oils, showed very much less penetration. From this result it is recognized that the tests may not be strictly comparative, as in some instances the films would stand out from the paper to a greater extent than in others. On account of this condition, it was suggested that the paper to be used for further tests be coated with a preparation that would be unacted upon by the paint or varnish liquids. Gelatin was proposed for this work. Due to its hygroscopicity and its possible effect upon film separation, it was found the paper might better be treated two or three days before testing, with a uniform coating of boiled oil, which acts as an insulating medium for the various

types of material under test. The first coating waterproofs the back of the paper, and renders it better suited for exposure. In some more recent tests the writer has secured the bond paper to small frames and then applied the coating to be tested.

In an effort to set a more exact requirement for "bending test" than that usually prescribed for varnishes, some of the coated papers were tested in the Schopper folding machine, so widely used for testing paper. The results were not satisfactory on paper coated on one face. With double coated paper or with stripped films this test might afford much information.

In studying the results of the tests referred to, the reader must be cautioned not to place too much emphasis on the differences shown by the various types of products. While it is undoubtedly true that certain indications are given by these tests, it would probably be better to await the developments of further work before accepting them as truly indicative of the results to be obtained on actual weathering of the same samples over long periods of time on a normal base, such as wood or metal.

Probably the most accurate device for determining the hiding power of liquid paints is that devised by Dr. Pfund. For full description see page 16. This instrument has found quite a wide application in the trade. An apparatus was designed along a somewhat similar principle by the present writer, but giving direct readings without manipulations of the clear glass cover top. It is free from the possible criticism of pigment accumulation at localized spots, due to working back and forth of the cover glass. The base of the apparatus (10 cm. in length and 2½ cm. wide) is of opaque white glass or of opaque black glass, according to whether white or colored paints are to be tested. At the end of the base is a metal piece made of German silver, permanently cemented on. This metal piece is 1 mm. thick. The surface of the glass base is divided into 10 equal parts, thus making the readings between each part 1/10 mm. A broad horizontal etched line passes down the middle of the glass base. The liquid paint to be examined is poured on the base, and the clear glass cover plate placed on the apparatus. The visibility of the longitudinal line disappears at a point between any two of the cross lines, which can be estimated in tenths of a division. The thickness of the paint at the point of hiding may therefore be directly read off in hundredths of a millimeter. Further experiments are being made to improve the apparatus.

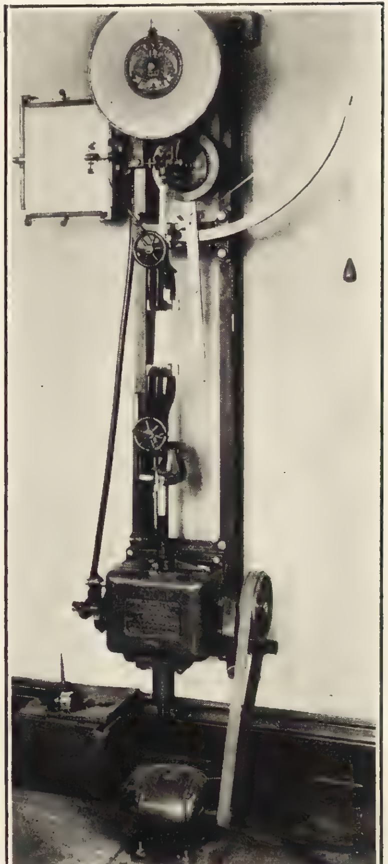

FIG. 3—Testing Paint Film on Paper for Tensile Strength

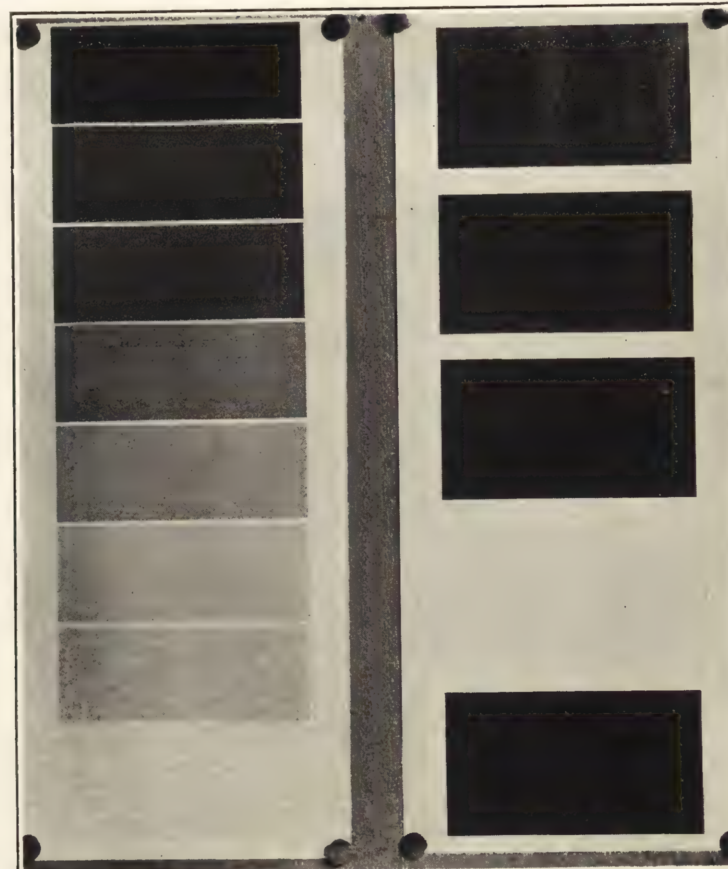

FIG. 4

Shaded Paper for Comparing Hiding Power of Paints

Color Block Paper for Varnish Liquids

TABLE I

Material.	Thickness of Coated Paper Inches.	Average Thickness.	Average Mullen Test.	Average Tensile Strength.	Appearance of Film After Exposure for Months.
H. Bond Paper Blank Test	.0032 .0032 .0033	.0032			Rough Dirty
Jan. 3			31	30	
Mar. 9			28	16	
RAW LINSEED OIL	.0042 .0038 .0040	.0040			Very Good Rather Dirty
Jan. 3			28	21	
Mar. 9			29	21	
BOILED LINSEED OIL	.0046 .0045 .0046	.0046			Very Good Rather Dirty
Jan. 3			31	23	
Mar. 9			32	26	
PREPARED PAINT OIL Boiled and Bodied Tung and Menhaden Type	.0047 .0046 .0048	.0047			Very Good
Jan. 3			37	20	
Mar. 9			37	23	
SYNTHETIC GARDOL Unsaturated Hydrocarbon	.0060 .0055 .0055	.0056			Good Rather Flat
Jan. 3			34	20	
Mar. 9			32	18	
ACETATE DOPE Navy Standard C. and R. Specification	.0033 .0034 .0035	.0034			Small Shrinkage Cracks
Jan. 3			33	36	
Mar. 9			32	33	
NITRATE DOPE Navy Standard C. and R. Specification	.0034 .0031 .0033	.0032			Great Shrinkage Cracks
Mar. 9			32	18	
Jan. 3			23	15	
D. BALLOON DOPE Navy Standard C. and R. Specification	.0035 .0030 .0035	.0033			Large Shrinkage Cracks
Jan. 3			33	27	
Mar. 9			24	15	
SPAR VARNISH No. 1	.0060 .0052 .0048	.0053			Excellent
Jan. 3			39	27	
Mar. 9			29	27	

TABLE I—*Continued.*

Material.	Thickness of Coated Paper Inches.	Average Thick-ness.	Average Mullen Test.	Average Tensile Strength.	Appearance of Film After Exposure for Months.
MARINE SPAR VARNISH	.0060 .0056 .0054	.0056			Excellent
Jan. 3			46	30	
Mar. 9			36	27	
RUBBING—POLISHING VARNISH	.0056 .0057 .0056	.0056			Shrinkage Cracks
Jan. 3			39	26	
Mar. 9			33	27	
CABINET RUBBING VARNISH	.0062 .0063 .0065	.0063			Shrinkage Cracks
Jan. 3			35	27	
Mar. 9			31	24	
MIXING VARNISH	.0050 .0056 .0052	.0053			Cracking and Flaking
Jan. 3			36	26	
Mar. 9			30	23	
FLOOR VARNISH	.0055 .0055 .0050	.0053			Very Good
Jan. 3			35	24	
Mar. 9			31	23	
100% White Lead	.0065 .0072 .0065	.0067			Very Good
Jan. 3			36	34	
Mar. 9			37	28	
75% White Lead 25% Zinc Oxide	.0068 .0068 .0067	.0067			Very Good
Jan. 3			36	29	
Mar. 9			41	30	
50% White Lead 50% Zinc Oxide	.0070 .0070 .0066	.0068			Very Good
Jan. 3			38	34	
Mar. 9			44	32	
25% White Lead 75% Zinc Oxide	.0065 .0066 .0066	.0066			Very Good
Jan. 3			39	34	
Mar. 9			45	32	

TABLE I—*Continued.*

Material.	Thickness of Coated Paper Inches.	Average Thickness.	Average Mullen Test.	Average Tensile Strength.	Appearance of Film After Exposure for Months.
100% Zinc Oxide	.0067 .0065 .0066	.0066			Very Good
Jan. 3			40	36	
Mar. 9			45		
EXTERIOR WHITE PAINT White Lead 50 Zinc Oxide 36 Asbestine 7 Barytes 7	.0082 .0086 .0073	.0080			Very Good
Jan. 3			44	40	
Mar. 9			46	32	
GLOSS WHITE Lithopone 75 Zinc Oxide 25	.0069 .0070 .0068	.0069			Very Good
Jan. 3			42	39	
Mar. 9			41	27	
INTERIOR WHITE ENAMEL No. 1 100% Zinc Oxide	.0059 .0061 .0062	.0060			Very Good
Jan. 3			41	34	
Mar. 9			43	23	
INTERIOR FLAT WHITE 100% Lithopone	.0063 .0068 .0055	.0062			Good
Jan. 3			36	28	
Mar. 9			29	31	
MARINE BLACK Spar Varnish 95% Carbon Black 5%	.0062 .0076 .0058	.0065			Very Good High Gloss
Jan. 3			32	33	
Mar. 9			38	29	
RED HOLD PAINT Iron Oxide in Thinned Spar Varnish	.0063 .0067 .0068	.0066			Good Rather Flat
Jan. 3			23	27	
Mar. 9			29	29	
RED PAINT Iron Oxide in Hydrocarbon Oil	.0056 .0058 .0058	.0058			Good Rather Flat
Jan. 3			28	17	
Mar. 9			30	23	
RED LEAD	.0070 .0080 .0083	.0077			Very Good
Jan. 3			40	33	
Mar. 9			45	32	

TABLE I—*Continued.*

Material.	Thickness of Coated Paper Inches.	Average Thickness.	Average Mullen Test.	Average Tensile Strength.	Appearance of Film After Exposure for Months.
RED SPAR	.0050				
Iron Oxide 20%	.0056	.0052			Very
Spar Varnish 80%	.0050				Good
Jan. 3	....		42	28	High Gloss
Mar. 9	....		38	28	

For determining the relative hiding power of liquid and also dry paint films, the writer has devised a rather simple method which uses a sheet of bond paper upon which squares of black, dark gray, light gray, and other graduated tints of gray are printed with wood blocks. These are lettered from A to H. After the sheets are furnished by the printer, they are kept in stock in the laboratory, and a brush coat of any experimental paint is applied in comparison with a standard product. While possibly subject to criticism from several angles, this method has been found satisfactory for general comparative work.

For the determination of the ageing properties of varnishes and other clear liquids, the writer has been using a sheet of paper upon which has been printed with blocks, squares of red, yellow, blue, and black. The varnishes applied over these surfaces in one or two-coat work are exposed on the roof of the laboratory or below a mercury arc lamp of the Uviol type. It has been found in tests of this character that varnish which stands up satisfactory over the white area may give unsatisfactory results over other colors and vice-versa. It is possible that this test may afford information as to the wearing value of a varnish to be used over coach or implement colors.

Ultra-violet Light.—Exposure of certain grades of lithopone to ultra-violet light will result in "fogging," the pigment turning gray. The test is usually applied to a water paste of the lithopone, complete "fogging" taking place in less than a minute with the more susceptible grades. The test applied to pigments of this character by The New Jersey Zinc Company laboratories is given below:

A sample of approximately three grams of lithopone is rubbed down to a stiff paste in three parts of China Wood Oil—rosin varnish containing lead dryer, and one part naptha. The

paste shall be spread on a porcelain palette, or a glass plate in a smooth, even layer which will not transmit light and is at least one inch by three inches in area.

The palette or glass plate shall be put in a warm place and the pastes dried until the glossy surface disappears. A strip of opaque black paper shall be laid across the samples to protect a portion of each from the light and the palette with the samples shall be immersed in water, allowing only a very thin film of water over the samples.

The standard time for exposure to good sunlight shall be two and a half hours and five minutes under an ultra-violet light.

Ultra-violet light is also utilized in making accelerated tests of paint.*

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* Accelerated Weathering of Paints. H. A. Nelson, Proc. A. S. T. M., 1922, Vol. XXII. Also Impermeability of Paint Films. A. M. Muckenfuss, *Ibid.*, 1914, Vol. XIV.

CHAPTER II.

PFUND PAINT TESTING INSTRUMENTS

Three valuable instruments for testing paints and pigments have been designed by Dr. A. H. Pfund, Associate Professor of Physics at Johns Hopkins University. They were originally described in the Journal of The Franklin Institute for November, 1919, March, 1920, and April, 1921. An abstract of these, as prepared by Dr. Pfund, together with additional comments by the writer and results obtained in this laboratory, are given below.

The Pfund Cryptometer.—This is an "absolute" instrument by means of which it is possible to determine the hiding power of a paint and of a pigment.

"Hiding power" may be defined as that property of a paint which enables it to obliterate beyond recognition any background upon which it may be spread. Since the color of the background affects the numerical value of the hiding power, a black background is chosen for white paints and, conversely, a white background for black paints. In the case of colored and gray paints, it will be necessary to carry out measurements for both types of background.

The idea underlying the construction of the cryptometer is this: granting that an infinitely thick layer of paint will hide a given background completely, it is sought to find the least thickness of paint which will be as effective in hiding as is the infinitely thick layer.

The form given the instrument is shown in Fig. 5. Here, *A* is a plate of black glass 14 × 5 × .6 cm. whose upper surface is optically flat. A transverse groove, *B*, about 2 mm. deep and 1 cm. wide, is cut in the upper surface and a millimeter scale is etched, as shown in the drawing. Resting upon plate *A* is plate *C* (7 × 3.5 × .6 cm.), whose lower surface is likewise optically flat. A strip of thin steel, *D*; 0.45 mm. thick, is attached to *C*, so that a wedge-shaped layer of white paint may be formed between the plates. This wedge terminates abruptly at the "infinitely thick" layer, *B*, and, so long as the hiding is not complete, the line of demarcation is visible. By sliding the wedge to the left it is finally impossible to see the edge. From a knowledge of the angle of the wedge and the reading on the scale, it is

possible to calculate the thickness of this critical layer lying immediately above the edge *B*. Now, in advancing the plate *C* until the line of demarcation can no longer be seen, we have overdone it, so to speak. To correct this, we must reverse the motion of the wedge until the edge can just be distinguished over its entire length. The mean value of the reading corresponding, respectively, to disappearance and appearance of the edge, yields the desired result. Since the fading away and reappearance is so gradual, due to the fact that the least perceptible increment of intensity which the human eye can detect is 1 to 2 per cent (Fechner's Law), it is clear that no high

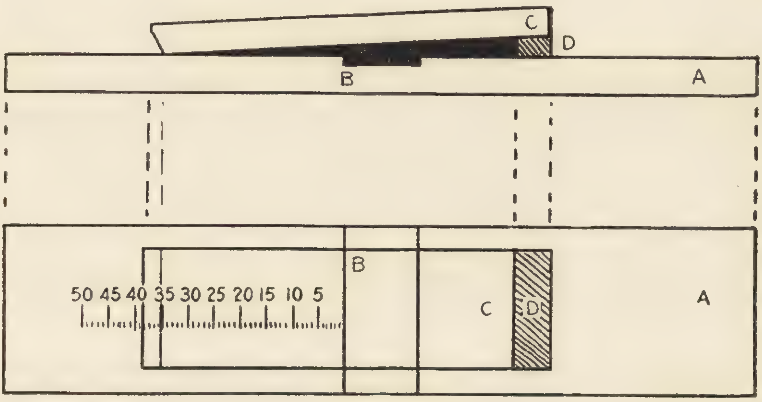

Fig. 5

degree of precision is attainable by this method. By taking ten pairs of readings it is found that the average deviation from the mean is about 5 per cent.

The hiding power of a paint may be obtained at once from a knowledge of the wedge-constant K (increase in thickness of paint film per unit linear advance along etched scale) and of l the wedge-reading at complete hiding. Lumping together the various numerical constants and recalling that l is measured in millimeters, it is possible to express the hiding power (H-P) of a paint by the simple relation:

$$\text{H-P} = \frac{40.7}{K\,l} \text{ square feet per gallon.}$$

A sharp distinction must be made between the hiding power of a pigment and that of a paint. Not only are these quantities expressed in different units, but they are not necessarily related in the sense that a pigment of great hiding power necessarily

produces a paint of correspondingly great hiding power. Taking up first the hiding power of pigments, let us consider an intimate mixture of x grs. of a white pigment and y grs. of colorless (or very pale) linseed oil. This mixture is tested in the cryptometer and the critical thickness producing complete hiding is found. Let

t=thickness of critical layer (in cms.).
b=numbers of grs. of pigment in a disc of 1 cm.² base and thickness t.

Then, if b grs. pigment hide 1 sq. cm., we find the number of sq. cm. A covered and hidden by 1 gr. of pigment from the relation

$$b : 1 :: 1 : A \text{ or } \frac{1}{b} = A.$$

Since the hiding power is better the thinner the layer, *i. e.*, smaller than b, we may define the hiding power of a pigment as the reciprocal of the number of grs. of pigment, mixed with colorless linseed oil to painting consistency, which are necessary to hide a black, non-absorbent area 1 sq. cm. This is numerically equal to the number of square centimeters covered and hidden by 1 gr. of pigment. Hiding powers of pigments will, therefore, be expressed in terms of sq. cm. per gr. The mode of calculating the hiding power of pigment and paint may, perhaps, best be illustrated by means of an actual determination:

Paint:

Basic Carbonate White Lead—72% by wt.—Density 6.81 Specific Vol. 0.147
Linseed Oil —28% by wt.—Density 0.92 Specific Vol. 1.08
Cryptometer constant K=0.0073
Cryptometer reading at complete hiding: l=25 mm.

$$72 \times .147 = 10.6$$
$$28 \times 1.08 = \frac{30.3}{40.9} \text{ c.c. paint contain 72 grs. pigment}$$
$$\frac{40.9}{72} = 0.567 \text{ c.c. contain 1 gr. pigment}$$
$$\frac{0.567}{K\,l} = \frac{0.567}{0.0073 \times 25} = 31.1 \text{ area covered by 1 gr. pigment}$$
$$\therefore \text{H-P (pigment)} = 31.1 \text{ cm}^2 \text{ per gr.}$$
$$\text{H-P (paint)} = \frac{40.7}{K \times l} = 223 \text{ sq. ft. per gal.}$$

These illustrations will suffice to show how calculations are carried out. A table of hiding powers, determined by this method, is presented elsewhere.

The Pfund Colorimeter for Nearly White Surfaces.—In view of the circumstances that ordinary colorimeters are entirely too insensitive and that visual estimates depend upon the character of the comparison surface, the present instrument was devised to yield quantitative colorimetric data for nearly white surfaces.

The idea underlying the construction is as follows: If we allow white light to fall upon a surface that is faintly greenish, the light reflected diffusely will contain a slight excess of green; if now this light be allowed to suffer reflection from a second surface, identical with the first, the light thus twice reflected will contain a greater percentage excess of green than before. By allowing, similarly, a third and a fourth reflection to take place, the accentuation of the green tint continues and finally becomes so pronounced that it may be measured readily. This is the method

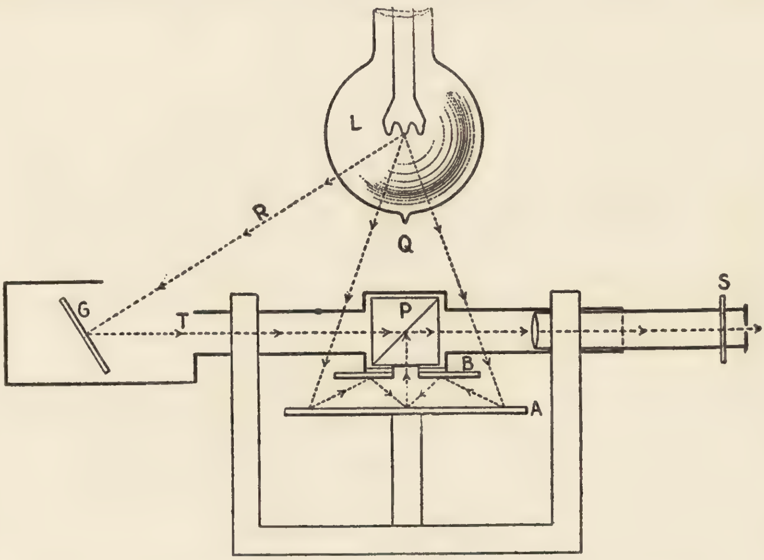

FIG. 6—Diagrammatic Representation of New Colorimeter

of "multiple reflections," according to which only truly non-selective (white or grey) surfaces leave the character of multiple reflected light unmodified. Any outstanding tint, however, is accentuated.

The apparatus as actually constructed is shown in Fig. 6. Here *L* is a powerful Mazda C lamp which illumines the outer portion of the circular disk *A*, whose upper surface is covered with the material to be studied. The light, diffusely reflected, illuminates the lower (similarly coated) surface of the disk *B* which, in turn, illuminates the central portion of the disk *A*. The light, after multiple reflections, passes upward through a central opening in *B* and is reflected horizontally by means of the photometer cube *P*. Another beam of light leaving *L* is reflected

from a disk of clear optical glass *G*, roughly ground on both sides. (Without going into details it may be stated that the most painstaking tests have shown that such a plate reflects visible radiations non-selectively.) This light passes through the tube *T* and fills the upper half of the field of view of the photometer cube which has a horizontal line of demarcation and which is viewed through a simple eye-piece yielding a linear magnification of 2.5. The intensity of this beam is varied by rotating the disk *G* about a horizontal axis. A pointer, attached to the rod bearing disk *G*, moves over a graduated scale which has been calibrated in terms of coefficients of diffuse reflections. The true values of such coefficients are first determined for a series of grey pastes (zinc oxide, glycerine, bone-black) of varying brightness by means of an absolute reflectometer. The colorimeter plates are then covered with these same pastes and scale-readings at photometric balance are recorded.

As a result of multiple reflections, the difference in scale reading corresponding to surfaces of slightly different brightness is about *four* times as great as it would have been had but a single reflection been used.

While this colorimeter lends itself admirably to the methods of monochromatic colorimetry, it has been found by actual experience that useful results are obtained more simply through the use of color-screens. Accordingly, color screens of dominant hue 480 $\mu\mu$ (blue), 540 $\mu\mu$ (green) and 605 $\mu\mu$ are successively placed in the eye-piece tube at *S* and photometric balances are established. The scale-readings thus obtaind are then evaluated into reflection coefficients by referring to the calibration curve. This is essentially a spectrophotometric procedure.

The final results are presented in the form of curves where abscissae represent wave-lengths of the color-screens and ordinates, reflection coefficients. A characteristic series of such curves applying to modern paint pigments will be presented elsewhere.

Hiding Power and Brightness of Pigments.—The writer secured from manufacturers, a series of white pigments representative of those produced in commercial quantities at the present time, and widely used in the industry. Portions of these pigments were submitted to Dr. A. H. Pfund who rubbed them up with glycerin and made careful measurements of their brightness, with the following result:

TABLE II—*Brightness of Various Pigments*

No.	Pigment	Coefficient of Diffuse Reflection ($MgO = 99.4\%$) Pigment in Glycerin		
		Blue $\lambda = 480\mu\mu$	Green $\lambda = 560$	Red $\lambda = 630$
1	Basic Sulfate—White Lead	81.2	87.6	89.3
2	Basic Carbonate—White Lead	79.8	82.7	84.7
3	Electrolytic White Lead	86.4	88.0	89.0
4	Old Process Lithopone	84.7	87.2	88.4
5	Leaded Zinc (35% Lead Sulfate)	78.4	82.7	85.2
6	Modern Process G. S. Lithopone	87.2	87.6	87.8
7	Modern Process K. L. Lithopone	88.9	88.2	88.2
8	Antimonious Oxide	86.4	89.0	90.1
10	Titanox (High oil absorption)	83.1	87.2	89.5
11	Titanox (Low oil absorption)	86.8	89.0	90.1
12	Zinc Oxide (French process)	88.2	88.9	89.5
13	Zinc Oxide (American Process)	82.7	86.0	86.8
14	Modern Process A. Lithopone	88.9	87.8	88.0
	Modern Process S. Lithopone (Regular)	86.6	88.7	89.7
	Modern Process S. Lithopone (Special)	88.4	87.8	87.4
	Modern Process G. S. Lithopone	88.4	88.2	88.0
	Modern Process A. Bk Label Lithopone	88.7	88.0	88.2
	Modern Process A. Bl Label Lithopone	88.7	88.2	88.4
	Modern Process P. L. R. Lithopone	89.5	88.4	87.8

Another series of these pigments was ground in a mill with refined linseed oil, on the basis of 50 parts by weight of pigment to 50 parts by weight of oil. These gave the following results in the writer's laboratory. See Table III.

It should be pointed out, however, that pigments of great briliancy, such as zinc oxide and basic sulphate-white lead, may show relatively low hiding power in their untinted condition. When slightly tinted with colors to match the color of leaded zinc or basic carbonate-white lead, they may show as great or even

TABLE III—*Hiding Power of Pigment-Oil Mixtures, Each Containing 50 Per Cent Pigment and 50 Per Cent Linseed Oil by Weight*

Paint No.	Pigment	Hiding Power Sq. Ft. per Gal.
1	Basic Sulphate—White Lead	116
2	Basic Carbonate—White Lead	145
3	Electrolytic White Lead	145
4	Old Process Lithopone	145
5	Leaded Zinc (35% Lead Sulphate)	200
6	Modern Process G. S. Lithopone	200
7	Modern Process K. L. Lithopone	200
8	Antimonious Oxide	193
10	Titanox (High oil absorption)	290
11	Titanox (Low oil absorption)	243
12	Zinc Oxide (French process)	215
13	Zinc Oxide (American process)	224
14	Modern Process A. Lithopone	200

greater hiding power than such pigments. Hiding power and brilliancy should, therefore, always be considered together.*

A third series was ground, using only sufficient oil to give the right consistency for brushing, as they would be used in paints. These were sent to Dr. Pfund who gave readings on his cryptometer, as shown in Table IV.

FOOTNOTE:

Results with the Pfund cryptometer on a large number of samples of each pigment examined by R. L. Hallett gave average general results as follows:

Hiding Power of White Pigments

	For complete hiding:					
	Sq. cm. per gram	Sq. ft. per lb.	Lbs. per 100 sq. ft.	Hid. Pow. weight	Hid. Pow. volume	Tint. Power
White lead	40	19.5	5.1	100	100	100
Basic lead sulphate	30	14.7	6.8	75	72	85
Titanox	80	39.0	2.6	200	128	350
Zinc oxide (American process)	46	22.4	4.5	116	96	170
Lithopone	50	24.4	4.1	125	80	200

* See J. Franklin Inst., Nov., 1919, p. 679. Also J. A. Calbeck's paper, "An Application of the Pfund Cryptometer," etc., Proc. Amer. Soc. Test. Mater., 1922.

TABLE IV—*Hiding Power of Pigment-Oil Mixtures Containing Different Amounts of Oil*

Paint No.	Pigment	Percentage By Weight As Determined By Analysis		Hiding Power	
		Pigment	Oil	Pigment Sq. Cm. per Gr.	Paint Sq. Ft. per Gal.
1	Basic Sulphate White Lead	69.7	30.3	25	159
2*	Basic Carbonate White Lead	70.4	29.6	36	242
3	Electrolytic White Lead	71.3	28.7	32	212
4	Old Process Lithopone	58.4	41.6	59	212
5	Leaded Zinc (35% Lead Sulphate)	63.6	36.4	49	252
6	Modern Process G. S. Lithopone	61.6	38.4	57	252
7	Modern Process K. L. Lithopone	58.4	41.6	58	232
8	Antimonious Oxide	64.5	35.5	44	232
10	Titanox (High oil absorption)	60.1	39.9	69	293
11	Titanox (Low oil absorption)	66.3	33.7	57	293
12	Zinc Oxide, French Process	50.2	49.8	44	142
13	Zinc Oxide, American Process	46.4	53.6	55	155
14	Modern Process A. Lithopone	59.1	40.9	54	212

* Note low luminosity of this sample in Table II which accounts for greater hiding power as compared to other lead.

The Pfund Paint-film Gauge.—This instrument was developed for the purpose of measuring the thickness of wet paint-films. Essentially, the instrument consists of a spherical, convex surface which is forced through the paint layer. Since the paint is a plastic solid whose "yield value" exceeds the existant capillary forces, the volume of paint originally in a circular disc of

section *ABCKA* is forced into the meniscus *AEFGBA*.. If the diameter (D) of the circular paint- spot is measured, and if the radius of curvature (R) of the convex surface be known, it is found that the thickness (t) of the original paint-film is given by the relation:

$$t = \frac{D^2}{16R}$$

The final form given the instrument is shown in Fig. 7. A convex lens L whose lower surface has a radius of curvature of 25 cm. is mounted in a short tube T, which slides freely in an outer tube T_2. The compression springs S keep the convex sur-

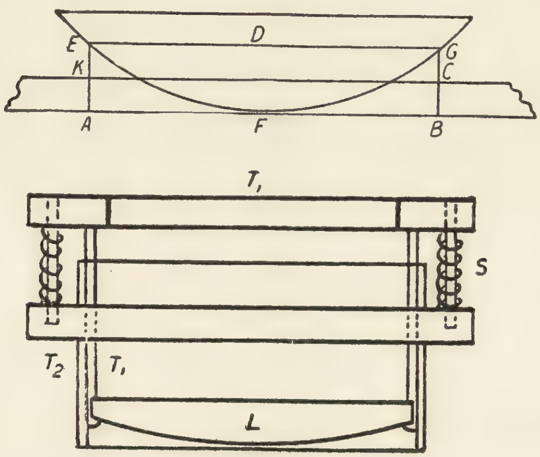

FIG. 7

face out of contact with the paint-film until pressure is applied to the top of T_1. This instrument is simply rested on a painted surface, and the lens is forced down as far as it will go. Upon releasing the pressure before removing the gauge, a circular spot is left on the gauge as well as on the painted surface. The diameter of the spot on the gauge is measured to 0.1 of a millimetre. If the spot is elliptical, the mean of the major and minor axes is determined. A series of readings on at least ten spots, judiciously distributed over a given area, yields a fair value of the average thickness of film. By referring to the table printed below, the thickness of the paint-film in mm. and the number of square feet which would be covered by one gallon of paint may be evaluated at once.

TABLE V

d = Diameter of paint spot on lens (in mm.).
t = Thickness of paint film (in mm.).

d In mm.	t Thickness in mm.	Sq. ft. per gal.
3	.00225	18,088
4	.00400	10,175
5	.00625	6,512
6	.00900	4,522
7	.01225	3,321
8	.01600	2,543
9	.02025	2,009
10	.02500	1,628
11	.03025	1,345
12	.03600	1,130
13	.04225	963
14	.04900	830
15	.05625	723
16	.06400	636
17	.07225	563
18	.08100	502
19	.09025	450
20	.10000	407
21	.11025	369
22	.12100	336
23	.13225	307
24	.14400	282
25	.15625	260
26	.16900	241
27	.18225	223
28	.19600	207
29	.21025	193
30	.22500	180
32	.25600	158
34	.28900	141
36	.32400	125
38	.36100	113

A number of experiments were carried out to check the accuracy of the paint-film gauge. In each case a known mass of paint was spread uniformly over a definite area of plate-glass, and the thickness of film was calculated in the usual manner. Different gauges and thickness of layer were used. The results are briefly presented in the following table:

	I	II	III	IV
Film thickness (by calculation)	0.0444 mm.	0.0402	0.0644	0.0638
Film thickness (by paint-film gauge)	0.0448	0.0390	0.0652	0.0638

Considering the roughness of the measurements, the agreement is surprisingly good. Equally satisfactory results were obtained on varnish films. The differences between the two sets of measurements rarely exceeded 3 per cent.

For testing the accuracy of this instrument, ideal conditions exist when the paint is grainless and the underlying surface is smooth, flat and non-porous. Using a zinc-oxide linseed-oil paint spread upon plate glass it has been found, as previously

noted, that the paint-film gauge yields results which are essentially correct. However, if the paint is gritty or if the surface to be painted is rough, the paint-film gauge will yield film thicknesses which are too small. Conversely, if the sub-surface is soft and yields under the pressure of the convex surface, the evaluated film thickness will come out too large.

Undoubtedly this instrument will be of great service to the paint experimenter in working on the physical properties of pigments.* Probably its most important application will be for gauging the thickness of coatings applied by the spray gun. Sprayed films are apt to be very thick unless the application is properly controlled. (See Table VI.)

The instrument is apparently accurate to within 25% of the correct value when applied to fairly smooth planes. This result was arrived at by the present writer† after several hundred tests upon a large number of paints applied to different kinds of surfaces. It should, therefore, be of interest to painters.

TABLE VI—*Measurements with Pfund Gauge on Surface Coated with a Spray Gun and Hand Brush*

	Tests on Wood. Spreading Rate, Sq. Ft. per Gallon.	Tests on Metal. Spreading Rate, Sq. Ft. per Gallon.
Mill White Primer:		
Hand Brush	868	1093
Spray	607	420
Mill White Flat:		
Hand Brush	1192	1107
Spray	382	557
Mill White Gloss:		
Hand Brush	1175	980
Spray	407	352

NOTE: Sprayed films were quite thick and had excellent hiding properties. Hand-brushed films were thin and more transparent.

Some of the factors which make the instrument not wholly reliable for measuring the thickness of films on exteriors are roughness of wood surfaces, rust spots on metal, slight splinters

* Readings on glass made with the Pfund gauge by P. R. Croll, New Jersey Zinc Co. Research Laboratories as referred to are 1047, 996, 979, 870 and 930 or an average of 964 as against a true spreading rate of 1009 square feet as determined by weight of paint (error 3.5 per cent.)

† See Circular 132 of the Scientific Section.

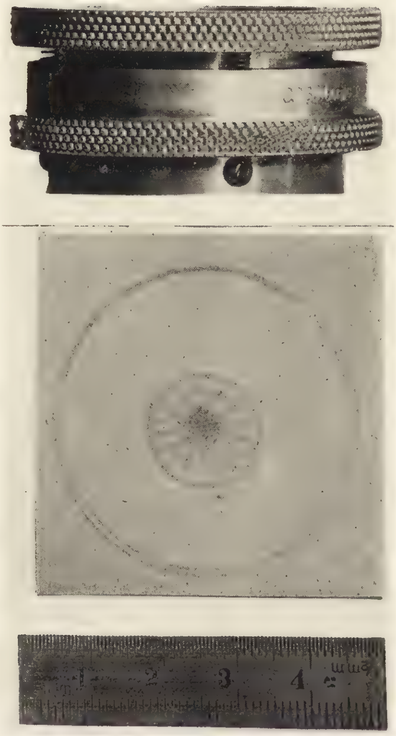

FIG. 8
Pfund Film Gauge
Mark Left on Painted Surface by Gauge
Scale for Measuring Spot on Gauge Lens

or grain effects on wood, coarse particles in paints that are not well ground, and yielding of surfaces under the pressure applied to the instrument.

A series of tests was also made to determine the actual ratio between spreading rate as calculated by determining the weight of a paint and the number of pounds or gallons applied to a surface, and the spreading rate as determined by the Pfund instrument. The measurements of the Pfund instrument were made upon the surfaces directly after the application of the paint. In these tests dressed lumber that had been primed, and perfectly clean black iron were used. Representative results are given herewith:

Wood.

Spreading rate estimated from weight of paint applied	815
Spreading rate by Pfund gauge	1175

Metal.

Spreading rate estimated from weight of paint applied	827
Spreading rate by Pfund gauge	1037

In another series of tests the following results were obtained:

TABLE VII

	Sprayed. Gauge Test.	Hand Brushed. Gauge Test.	Hand Brushed. Actual spreading Rate Estimated from Weight of Paint Applied.
Mill White Primer:			
Glass	1088	1160	....
Iron	925	1001	1073
Wood	670	755	885
Gloss White:			
Glass	1370	1068	....
Iron	925	1052	1017
Wood	510	686	868

In the above tests at least ten measurements were made with the Pfund instrument on each test, and the average figure used in calculating the thickness of the films. It is of interest to note the rather uniform results obtainable in hand-brush application, as shown by the measurements below.

TABLE VIII—*Diameter of Spot in Centimeters*

Paint No. 1.	Paint No. 2.	Paint No. 3.	Paint No. 4.
1.25	.87	1.45	1.30
1.30	.87	1.45	1.25
1.10	.90	1.45	1.22
1.12	.90	1.40	1.22
1.05	.90	1.45	1.20
1.05	.90	1.40	1.25

Apparently from the above results, the gauge may either overestimate or underestimate the amount of paint applied. It is believed, however, that the instrument will be found of considerable use in painting work.

CHAPTER III.

DETERMINING THE SPECIFIC GRAVITY OF PAINT PIGMENTS

There is given below the method developed and standardized in the writer's laboratory for the determination of the specific gravity of paint pigments. This method was originally published in Circular No. 104.

1. *Standardization of Pyknometers.*—Fill the pyknometers with freshly-boiled distilled water and bring to temperature of 15.6° C. Dry and weigh as outlined in paragraph 6. Clean, weigh and dry the pyknometers. Fill them with the kerosene to be used and bring to temperature of 15.6° C. Dry and weigh in the same manner. Calculate the specific gravity of the kerosene by dividing the weight of water into the weight of kerosene.

2. *Drying.*—Dry the pigment in an oven, preferably electric, at 105° C. for 2 hours.

3. *Weighing.*—Weigh a sample of the pigment, by difference, in the weighing bottle. For blacks, blues, and lakes of light specific gravity, use about 1 gram; for inert crystalline pigments, about 4 grams; for opaque white pigments, 7 to 10 grams; for red lead, 15 to 20 grams. Due to the hygroscopic nature of some of the pigments it is necessary to use a weighing bottle fitted with a cork stopper.

4. *Transferring to Pyknometer.*—Pour sufficient kerosene into the pyknometer to form a quarter of an inch layer in the bottom and add a quantity of pigment from the weighing bottle reaching approximately three-quarters of the distance to the kerosene level. The kerosene should always cover the pigment. Stir the sample with a polished round bottom glass rod until completely covered by the kerosene, if necessary adding more kerosene from the wash bottle. Wash rod with kerosene.

5. *Removal of Occluded Air.*—Place the pyknometers in the desiccator, which should then be closed and attached to the water pump until the greater part of the air is expelled from the system. This takes from 5 to 10 minutes. Close the system with a pinchcock and attach the desiccator to an oil pump for the removal of the small amounts of air given off at the low pressures obtainable with the oil pump. The manometer is used to indicate whether the oil pump is giving the proper vacuum.

When the manometer indicates that the vacuum, which should be not greater than 3 millimeters, is constant, the oil pump may be cut off for short periods, precaution being taken that the vacuum does not change materially due to leakage. It will be noticed that bubbles of air come from the pigments very rapidly at first and that this action gradually decreases and finally stops altogether. The time required for complete removal of air varies from one-half hour to two hours, depending upon the nature of the pigment. When no more bubbles can be seen it is assumed that all the occluded air has been given off and

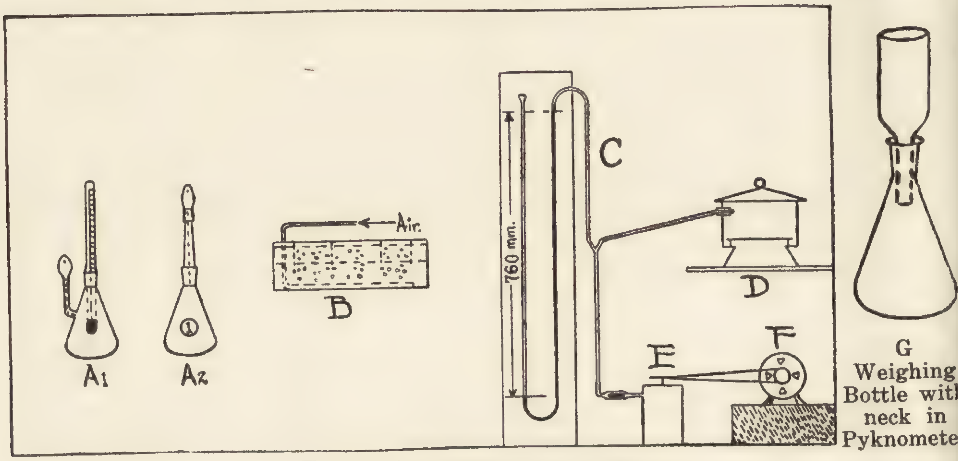

FIG. 9—Apparatus Used in Work

the pigment thoroughly wet with kerosene. Air can then be slowly admitted to the desiccator by means of the pinchcock.

6. *Filling and Bringing to Temperature.*—Take the pyknometer from the desiccator and fill with kerosene, care being taken to add sufficient to prevent the formation of air bubbles when placement of the thermometer is made. Place the thermometer in the water bath. Cool the bath with ice to between 10 and 13° C. Place the pyknometer in the bath and allow it to come to constant temperature. Insert the pyknometer thermometer or capillary tube. Add enough warm water to the bath to raise the temperature suddenly to about 14.5° C. in order to expand the kerosene and prevent it from creeping down the capillary and admitting a small amount of air. Allow the bath to come to a temperature of 15.6° C. Wipe the capillary tube with filter paper and put on the cap. Read all temperatures on the thermometer in the bath and not on the thermometer in the pyknometer. Remove the pyknometer from the bath and dry.

Allow it to stand for one-half hour to enable it to come to room temperature. Weigh. It is advisable to allow pyknometer to stand approximately the same time before each weighing so as to compensate for slight errors due to evaporation at the joints.

7. *Precautions.*—Before a new desiccator is first used it should be wrapped in a towel and tested under the vacuum to be used. Great care should be exercised in handling the desiccator when the vacuum is on, as any sudden jar may cause it to collapse.

8. *Number of Samples.*—It has been found convenient to run six samples at one time, the desiccator specified being of the proper size to accommodate the above number.

DESCRIPTION OF APPARATUS USED IN METHOD.

A. Pyknometer.	Capacity 50 CC.
Type A1.	Thermometer at neck, and capillary tube at side. A. H. Thomas Co. No. 46688. Central Scientific Co. No. 1730.
Type A2.	Long, thin capillary tube at neck. Specially made by Eimer and Amend.
B. Water Bath.	Vessel filled with sufficient water to permit of only a very gradual rise in temperature. Equipped with a stirring device, preferably air blown, as the pyknometers are easily tipped over.
C. Manometer.	Open tube Manometer to show vacuum obtained in desiccator. Made of 6 mm. diameter glass tubing filled with mercury to approximately 86 cm. fitted with pressure tubing attached to a Y tube leading to desiccator and pump.
D. Desiccator.	Heavy Wall Glass Desiccator constructed for vacuum work, with hole at side. To withstand vacuum of one atmosphere. A. H. Thomas Co. No. 25834. Scientific Materials Co. No. 1919. Central Scientific Co. No. 3776.
Water Pump.	Laboratory water vacuum pump necessary to expel the greater portion of air in the desiccator. Scientific Materials Co. No. 2554, No. 2556. Central Scientific Co. No. 5476.
E. High Vacuum Pump	Small vacuum pump to give vacuum of not more than 3 mm. The Nelson Oil Pump is satisfactory. This pump has a displacement of approximately 200 cubic inches per minute or 7 cubic feet per hour at a speed of 900 R.P.M. It will evacuate a flask of one liter capacity to a vacuum of 1 mm. in two minutes. Scientific Materials Co. No. 143.
F. Electric Motor.	To drive Vacuum Oil Pump. A constant speed type of motor is most satisfactory. If for D. C., a shunt wound motor, or, if for A. C. an induction motor. The most efficient speed is between 800 and 900 R. P. M. At this speed it gives as good results as when driven faster, and develops less heat.
G. Weighing Bottle.	Weighing Bottle with cork. Neck to be small enough to fit inside the neck of the pyknometer. This is essential, as small quantities of pigment easily adhere to the ground glass joint of the pyknometer. 25 c.c. Babcock Milk Test Bottles are satisfactory after cutting off the neck to approximately 1½ inch. A. H. Thomas Co. No. 33964. Scientific Materials Co. No. 4176. Central Scientific Co. No. 9104.

Thermometer. Range 0° to 60° C. graduated in 1/10ths of a degree.
Wash Bottle. Ordinary water bottle type for kerosene.

NOTE: The difference in levels of the mercury in the manometer when the system is in operation, subtracted from the barometer reading taken at the same time, gives the vacuum of the system in millimeters of mercury. The difference between the barometer and the manometer should not exceed 3 MM.

EXAMPLE OF CALCULATIONS

Standardization of Pyknometer

Weight of bottle and water	= 88.2777
Weight of bottle.........	= 33.3527
Weight of water at 15.5° C.	= 54.9250
Weight of bottle and kerosene	= 77.9420
Weight of bottle..............	= 33.3527
Weight of kerosene at 15.5° C.	= 44.5893

$$\text{Specific gravity of kerosene}_{15.5^\circ\text{ C.}} = \frac{\text{Weight Kerosene}}{\text{Weight Water}} = \frac{44.5893}{54.9250} = .8118.$$

METHOD OF CALCULATING RESULTS

Let K = Weight of bottle filled with kerosene only.
Let P = Weight of pigment used.
Let F = Final weight of bottle with pigment and kerosene.
Let S = Specific gravity of the kerosene used.

$$\text{Then specific gravity of pigment} = \frac{P \times S}{(P + K) - F}.$$

Thus:

Red Lead

K = Weight of bottle filled with kerosene only = 77.9420.
P = 16.0000.
F = Final weight of bottle with pigment and kerosene = 92.4826.
S = .8118.

$$\text{Sp. Gr. of sample Red Lead} = \frac{16.0000 \times .8118}{(16.0000 + 77.9420) - 92.4826} = 8.90.$$

METHOD FOR DETERMINING SPECIFIC GRAVITY OF PAINT LIQUIDS

The specific gravity of a liquid may be determined with sufficient accuracy with a Westphal balance or a standardized hydrometer and thermometer in the customary manner, making any necessary corrections for temperature. For viscous blown or bodied oils or for mixed paints, satisfactory results may be obtained, when a quantity is available, by weighing a liter of the oil or paint in a graduated tared liter flask. When only small amounts are available or when great accuracy is desired the method below* should be used:

* The above described method is adopted from the proposed tentative standard test for the specific gravity of road oils, road tars, asphalt cements, and soft tar pitches. See Proc. Amer. Soc. Test. Mater., Vol. XX, 1920.

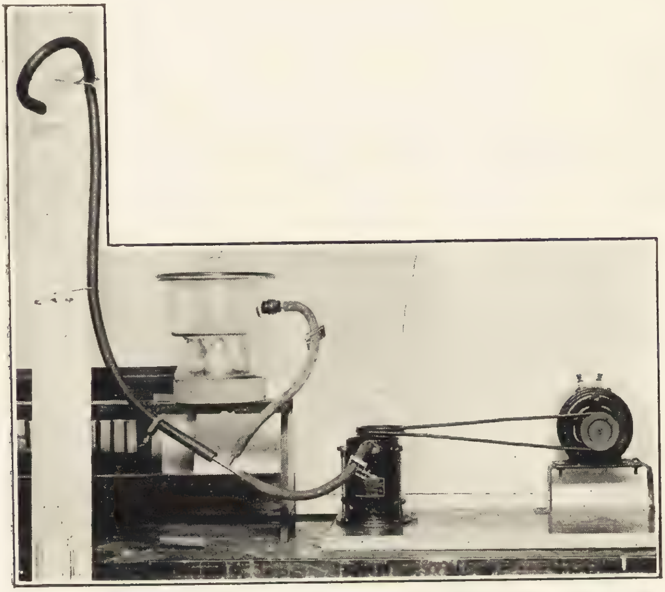

FIG. 10—Photo of Apparatus

The specific gravity of an oil is expressed as the ratio of the weight of a given volume at 25° C. to that of an equal volume of water at the same temperature. The determination of specific gravity, in the case of heavy bodied oils especially, is best made in a straight walled glass tube pyknometer approximately 70 mm. long and 22 mm. in diameter, carefully ground to receive an accurately fitting glass stopper with a hole of 1.5 to 1.7 mm. bore in place of the usual capillary opening. The stoppered tube should have a capacity of about 24 cc., and when empty should weigh not over 35 grams.

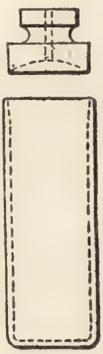

FIG. 11—Pyknometer or weighing bottle.

The type of bottle described is illustrated.

The pyknometer with stopper is first calibrated by weighing it, clean and dry, upon an analytical balance. This weight is called A. It is then filled with distilled water at a temperature of 25° C., the stopper firmly inserted, all surplus moisture wiped from the surface with a clean, dry cloth, and again weighed. This weight is called B.

For the determination of the specific gravity of an ordinary oil or paint liquid, the material shall be brought to a temperature of 25° C. and poured into the pyknometer until it is full, using care to prevent the inclusion of air bubbles. The stopper is then inserted and the excess of liquid forced through the opening is carefully removed with a clean, dry cloth. The pyknometer and contents are then weighed, and this weight is called *C*. The specific gravity of the material may then be calculated from the following formula:

$$\text{Specific gravity} = \frac{C - A}{B - A}$$

When the specific gravity of extremely heavy bodied oils or blown oils, or certain paste products is to be determined, the viscosity of these materials may make the previously described method inapplicable. Such materials should first be gently warmed, using care to prevent loss by evaporation. When fluid, enough is poured into the clean, dry pyknometer to about half fill it. Precautions shall be taken to keep the material from touching the sides of the tube above the final level and to prevent the inclusion of air bubbles. It is advisable to slightly warm the tube before filling. The pyknometer and contents are then cooled to room temperature and weighed with

the stopper. This weight is called C. The pyknometer is next removed from the balance, filled with distilled water, and the stopper firmly inserted. It is then completely immersed for not less than 30 minutes in a beaker of distilled water maintained at 25° C., after which it is removed and all surplus water wiped off with a clean cloth. It is immediately weighed. This weight is called D. The specific gravity of the material may be calculated from the following formula:

$$\text{Specific gravity} = \frac{C - A}{(B - A)\ \ (D - C)}.$$

Average Specific Gravity Data.—For the convenience of manufacturers who do not have facilities for making specific

TABLE IX—*Table of Bulking Averages—Specific Gravity of Paint Liquids*

	Specific gravity.	Weight per solid gallon.	One pound bulks gallons.
Raw Linseed Oil	.932	7.764	.1288
Boiled Linseed Oil	.942	7.847	.1274
Heavy Bodied Linseed Oil	.98	8.163	.1225
Raw Soya Bean Oil	.929	7.739	.1292
Raw Tung Oil	.940	7.830	.1277
**Liquid Paint Drier	.85	6.681	.1497
**Mixing Varnish	.905	7.539	.1326
Turpentine	.867	7.222	.1385
**Mineral Spirits	.775	6.456	.1549
Benzol (90%)	.882	7.347	.1361
Benzine (62°)	.745	6.206	.1611
Solvent Naphtha (160°)	.902	7.514	.1331
Grain Alcohol	.785	6.539	.1529
Wood Alcohol	.791	6.589	.1518
Acetone	.797	6.639	.1506
Carbon Tetrachloride	1.60	13.328	.07502
Amyl Acetate	.874	7.280	.1374
Ethyl Acetate	.902	7.514	.1331

** These liquids will vary greatly in specific gravity. Grinders should determine the figure for the products they use.

gravity determinations on various types of pigments, and who desire a chart showing the average specific gravity of many of the commonly used pigments, a special table has been prepared. It should be pointed out, however, that the specific gravity of even such colors as are termed chemically pure, such for instance as chrome green, may vary to a great extent. This is due to the fact that these greens may contain a small or a large percentage of blue, and in some instances varying amounts of lead sulphate. This variance in composition, therefore, of even

chemically pure colors, is sufficient to warn the paint grinder that serious mistakes may occur in calculations made on average specific gravity figures of certain colored pigments. A chart is also presented showing the specific gravity and bulking values of many liquids that are used in paint and enamel manufacture.

TABLE X—*Table of Bulking Averages—Specific Gravity of Dry Pigments*

	Specific gravity.	Weight per solid gallon.	One pound bulks gallons.
Basic Carbonate White Lead	6.81	56.73	0.01763
Basic Sulphate White Lead	6.41	53.40	.01873
Zinc Oxide	5.66	47.15	.02121
Zinc Oxide, Leaded 35%	5.95	49.56	.02018
Lithopone	4.30	35.82	.02792
Titanox	4.30	35.82	.02792
Asbestine	2.85	23.74	.04212
Barytes	4.45	37.07	.02698
China Clay	2.62	21.82	.04583
Silica	2.65	22.07	.04531
Talc	2.84	23.66	.04227
Whiting	2.71	22.57	.04431
*Venetian Red, (20% Fe_2O_3)	3.05	25.41	.03935
Red Oxide, (40% Fe_2O_3)	3.45	28.74	.03479
Red Oxide, (95% Fe_2O_3)	4.95	41.23	.02425
Indian Red, (90% Fe_2O_3)	4.92	40.98	.02440
Ferric Oxide, (98% Fe_2O_3)	5.15	42.90	.02331
Tuscan Red	3.95	32.90	.03040
Ochre	2.80	23.32	.04288
Sienna, Raw	3.27	27.24	.03671
Sienna, Burnt	3.95	32.90	.03040
Umber, Raw	2.68	22.32	.04480
Umber, Burnt	3.80	31.65	.03160
Brown Oxide, (50% Fe_2O_3)	3.35	27.91	.03583
Mineral Brown, (45% Fe_2O_3)	3.34	27.82	.03595
Chromium Oxide	4.95	41.23	.02425
Litharge	9.40	78.30	.01277
Orange Mineral	8.80	73.30	.01364
Red Lead	8.80	73.30	.01364
Pure Para Toner	1.50	12.50	.0800
Para Red 10% (on Lime and Barium Base)	2.65	22.07	.04531
Pure Toluidine Red Toner	1.49	12.41	.08058
*Chrome Green, C. P	*3.90 *5.08		
Green Earth	2.75	22.91	.04365
Limeproof Green	2.80	23.32	.04288
American Blue	1.85	15.41	.06489
Ultramarine Blue	2.35	19.58	.05107
*Chrome Yellow, C. P	*6.00		
Lampblack	1.78	14.83	.06743
Carbon Black	1.81	15.08	.06631
Drop Black	2.64	21.99	.04548
Graphite	2.36	19.66	.05086
Keystone Filler	2.71	22.57	.04431
Zinc Dust	7.06	58.81	.01700
Aluminum Dust	2.64	21.99	.04548
Lead Dust	11.09	92.38	.01082

* These will vary widely according to composition required for shade or tone and character of base.

EXAMPLES OF FIGURING BULKING VALUES OF PAINT FORMULAS.—*Example I*

Pounds	Specific gravity of material	One pound bulks gallons	Poundage used bulks gallons	Material invoice cost per pound	Material invoice cost pounds used
Pigment 64 %					
19 Basic Carbonate White Lead	6.81	0.01763	0.334		
19 Basic Sulphate White Lead	6.41	.01873	.355		
19 Zinc Oxide	5.66	.02121	.402		
7 Barium Sulphate	4.45	.02698	.188		
Liquid 36 %					
30 Linseed Oil	.932	.1288	3.864		
3 Mineral Spirits	.775	.1549	.464		
3 Drier	.802	.1497	.449		
100 lbs.			6.056 gals.		

Gallons bulked 6.056
Weight per gallon . . . . . . 16.5 lbs.
Raw material cost per gallon . . . . . .

From the above figures Deduction for Volatile and Grinding Loss should be made.
To the above figures Cost of Cans and Cases should be added
To the above figures Manufacturing Costs should be added
To the above figures Selling Price over Factory Cost should be added.
To the above figures Net Profit on Sales should be added.

} See Report of Cost Accounting Committee.

Example II

Pounds	Specific gravity of material	One pound bulks gallons	Poundage used bulks gallons	Material invoice cost per pound	Material invoice cost pounds used
275 Basic Carbonate White Lead	6.81	0.01763	4.85		
275 Basic Sulphate White Lead	6.41	.01873	5.15		
300 Zinc Oxide	5.66	.02121	6.36		
100 Silica	2.65	.04531	4.53		
25 Whiting	2.71	.04431	1.11		
442 Raw Linseed Oil	9.32	.1288	56.93		
40 Bodied Linseed Oil	9.86	.1225	4.90		
15 Drier	8.02	.1497	2.25		
12 Mineral Spirits	7.75	.1549	1.86		
15 Water Solution	1.00	.1200	1.80		
1499 lbs.			89.74 gals.		

Gallons bulked 89.74
Weight per gallon . . . . . . 16.7 lbs.
Raw material cost per gallon . . . . . .

From the above figures Deduction for Volatile and Grinding Loss should be made.
To the above figures cost of Cans and Cases should be added.
To the above figures Manufacturing Costs should be added.
To the above figures Selling Price over Factory Cost should be added.
To the above figures Net Profit on Sales should be added.

} See Report of Cost Accounting Committee.

Example II is similar to a formula recently sent out to various grinders for bulk estimations, except that the liquid components vary slightly. For grinders who still base their batches on gallonage rather than poundage of liquids, the poundage can be obtained from the weight per gallon.

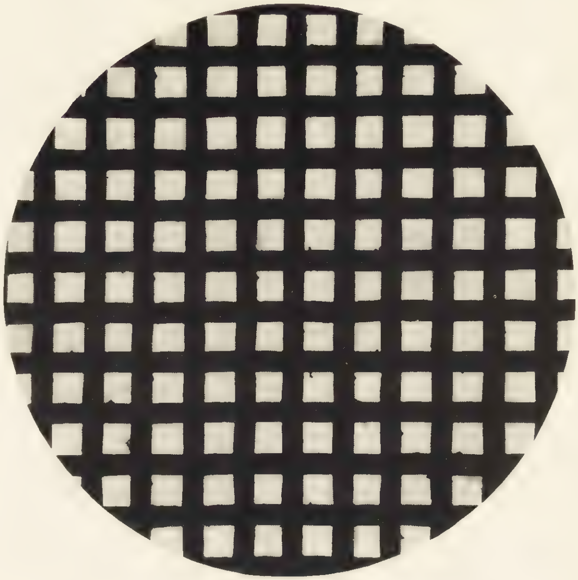

FIG. 12—Standard 200-Mesh Screen X-50
Unused

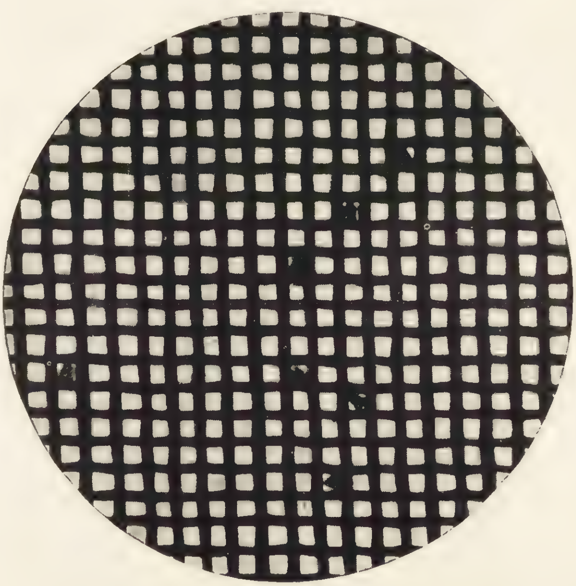

FIG. 13—Standard 325-Mesh Screen X-50
Used 4 Times. Note Pigment Particles Retained

CHAPTER IV.

DETERMINING THE FINENESS OF PAINT PIGMENTS

There is given below the method developed and standardized in the writer's laboratory for the determination of the fineness of paint pigments. This method was originally published in Circular No. 148.

(*a*) Reserve in the laboratory a standard 325-mesh screen for comparison purposes. Whenever a new screen is secured, a practical test of its accuracy should be made by running on it and on the standard screen a pigment that has a considerable percentage of coarse particles. A reserve stock of such pigment should be kept for this purpose.

(*b*) Weigh the screen upon an analytical balance, recording the weight in a figure carried to the third decimal place. Then wet the screen on both sides with the liquid to be used for wash purposes.

(*c*) Weigh upon a piece of paper or a tared watch glass, a sample of the pigment to be tested. For most pigments 10

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* Sieves 3 inches in diameter will be received by the Bureau of Standards for test. The cloth will be tested to determine whether or not it conforms to the specifications for cloth of the U. S. Standard Sieve Series. The specifications for the sieve frame are now being prepared. No. 325 cloth of the U. S. Standard Sieve Series should be made of wire 0.036 mm. (0.0014 inch) in diameter, a tolerance of 20 per cent being allowed at present for this diameter. The average opening between adjacent parallel wires should be 0.044 mm. (0.0017 inch) the tolerance being 7½ per cent with the additional limitation that the maximum opening shall not exceed 0.044 mm. by more than 60 per cent. Sieves whose cloth conforms to these specifications and whose frames are in accordance with specifications now in preparation will be marked with the letters "BS" and the year in which the test is made. A report will be issued for each sieve submitted, a nominal fee being charged for this test.

For those who desire to investigate the subject further the following references are given:

The classification of Fine Particles According to Size. By G. W. Thompson, Proc. A. S. T. M., Vol. X, 601 (1910).

Kolloid Zeitschrift. Vol. 18, page 3348, 1916.

Rapid Test for Fineness of Paint Pigments. By Dr. C. D. Holley and J. C. Brier. Drugs, Oils and Paints, May 10, 1915.

Comparative Tests for Fineness of Pigments. By Dr. C. D. Holley. Paint, Oil and Chem. Review, No. 23, 1921.

Circular No. 90. By H. A. Gardner, Scien. Sec., Educat. Bur., Paint Mfrs. Assn. U. S.

A Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments. By Henry Green, J. Franklin Inst., 192,637 (1921).

See also "Optical Properties of Pigments," H. E. Merwin. Proc. A. S. T. M., Part II, 1917, page 496.

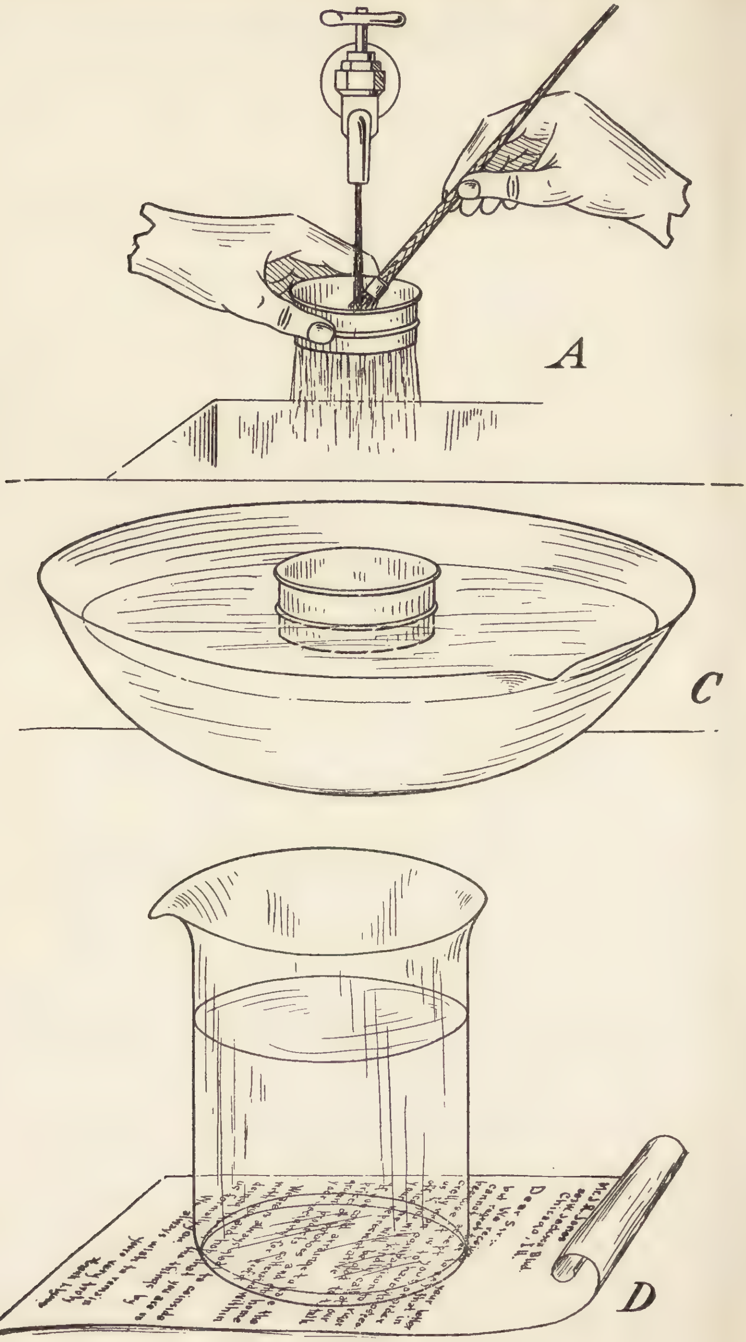

FIG. 14

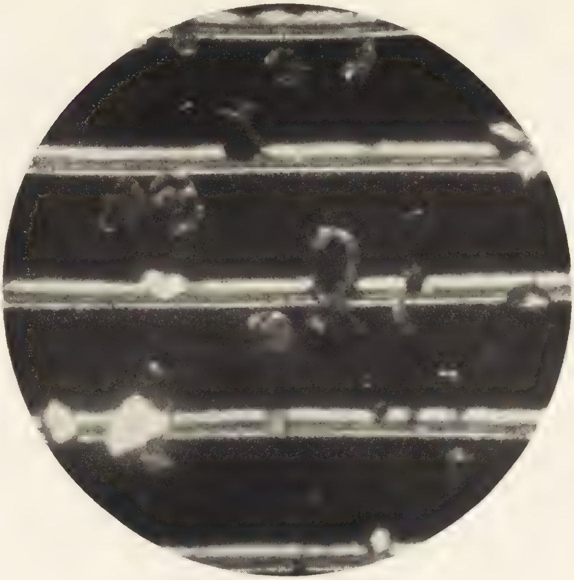

FIG. 15—Red Lead
Some Particles Are Transparent

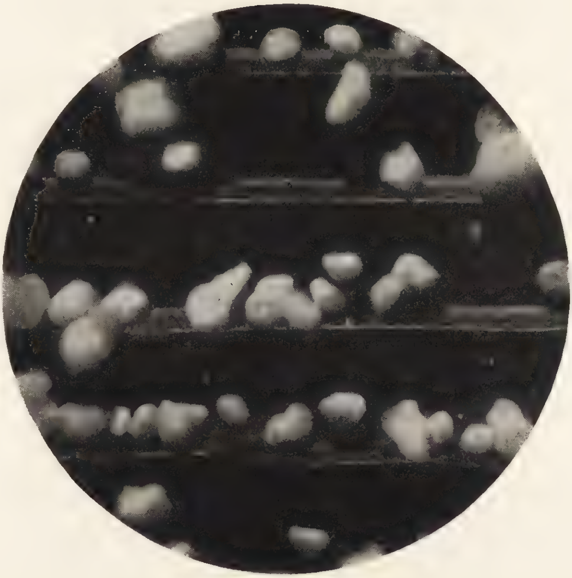

FIG. 16—White Lead

grams will be the proper quantity. For black pigments of low specific gravity, 2 grams will be sufficient. For pigments like Prussian blue and graphite, 3 grams are generally used. The pigment may then be transferred to the screen.

If the pigment is one that is difficult to wet with the wash liquid, the quantity weighed out should first be placed in a beaker containing some of a liquid that easily wets the pigment and

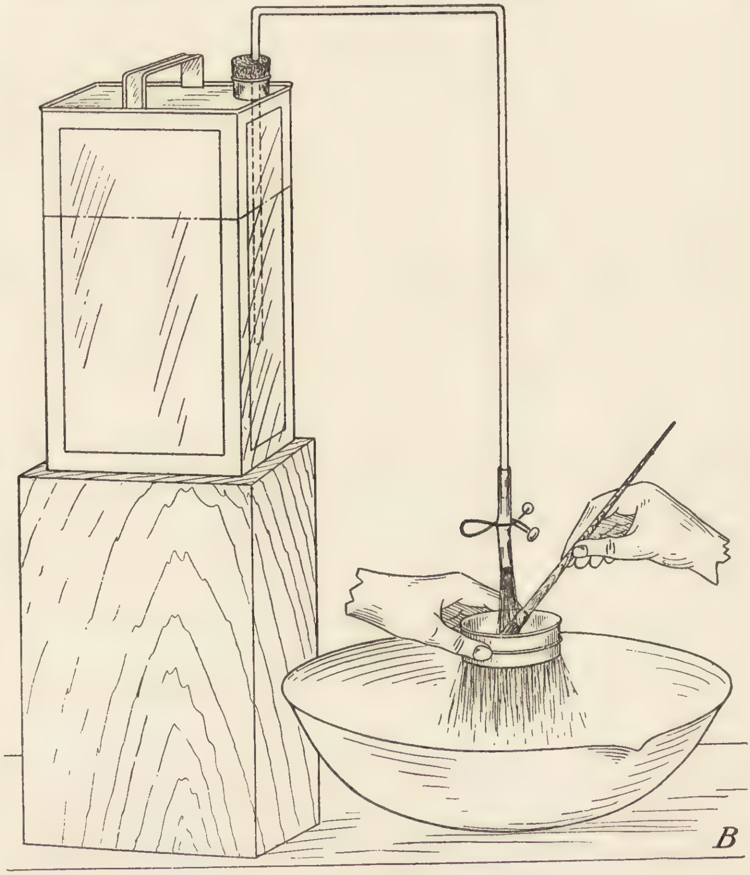

FIG. 17

that is miscible with the wash liquid. For instance, if water is to be used as the wash liquid, alcohol may be used as the wetting medium. The pigment is then gently stirred with the wetting liquid and the contents of the beaker transferred to the screen. Where small particles of pigment are retained on the stirring rod or walls of the beaker they may easily be removed with the brush.

(*d*) The screen is then held under a tap (A) delivering about 300-500 cc. of wash liquid per minute. By slightly shaking the screen, the pigment will be rapidly carried through. A soft camel's hair brush may be used in aiding the operation. If the screen is held at a slight angle so that the pigment will gradually collect at one edge during the washing process, and then rotated, the pigment may be brushed out rapidly, with no risk of clogging the screen.

(*e*) After the majority of the finely divided portion of the pigment has passed through the screen (from two minutes to an hour, according to kind of pigment), the screen is placed in an 8-inch porcelain dish (C) containing 250 cc. of the wash liquid. The screen will thus be covered to a depth of about one-half inch. The pigment remaining on the screen may be brushed with a soft 1-inch camel's hair brush at the rate of two strokes per second during two periods of 10 seconds each. The screen is then raised from the dish after each 10-second period to let the liquid on the screen run through. Change the liquid in the dish after every two brushing periods described above. Continue this operation until typewritten letters can be read through a layer of the wash liquid 8 cm. thick, which is approximately the height of a filled 250 cc. beaker of the usual laboratory type (D).

Occasionally pigments will be found that foam when water is used as the wash liquid. In such instances, during the last washing in the porcelain dish, the use of a liquid that breaks down the foaming and is readily miscible with water, such as alcohol, will usually overcome this difficulty.

(*f*) Now wash back on to the screen the pigment particles adhering to the brush. Wipe off the water below the screen. Add a few drops of alcohol and then of ether to expedite drying. Dry the screen in a water bath or on a radiator, and weigh.

(*g*) For pigments requiring wash liquids such as turpentine or mineral spirits, use apparatus shown in (B). This apparatus is also used for determining the fineness of paste paints ground in oil. For paints containing varnish, such for instance as Japan colors, a wash liquid of turpentine, solvent naphtha or similar solvents is necessary depending on type of pigment and varnish. Always finish with ether to remove traces of heavy wash liquids such as turpentine which might dry to resinous film.

Discussion of Method.—A slight source of error in the above

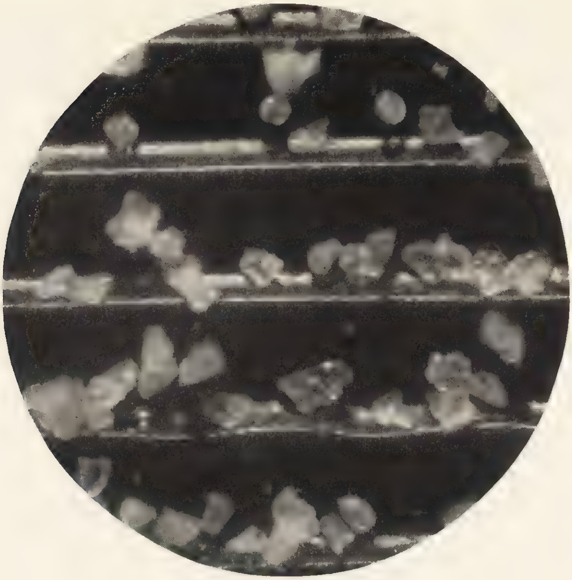

FIG. 18—Barytes

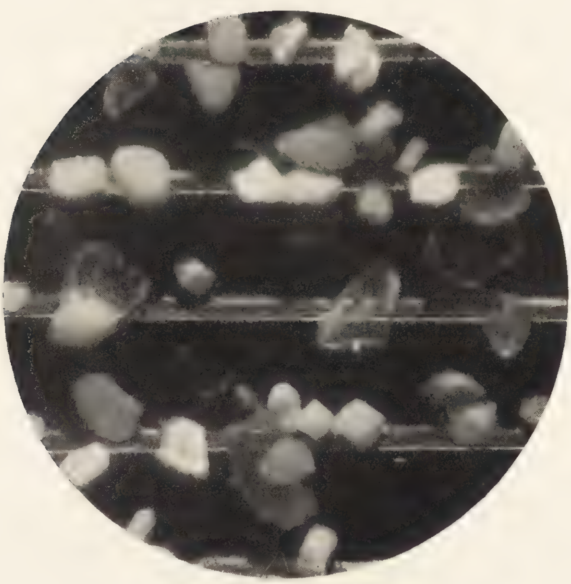

FIG. 19—China Clay
Note Transparent Particles

method may result from the fact that the opacity of a small quantity of pigment in the wash liquid is dependent not only on the optical constants of the pigment and liquid but also on the size of the particles. In other words, a certain degree of opacity may be produced by varying the amount of pigment. However, the error has been found to be extremely slight, and the method is very much more rapid than that at one time suggested, of drying and weighing the screen at a number of intervals during the brushing operation, to constant weight. This latter method would be very tedious and cause great loss of time.

Occasionally pigments will be found that contain quantities of soft lumps or aggregates of finely divided particles which have been cemented together by moisture or by over-heating during the drying process. All of these lumps will not pass through the screen even with brushing, as the brush is too soft to break down the aggregates. Placing these lumps between the fingers and exerting slight pressure on them will readily indicate whether they are single coarse particles or aggregates of fine particles which may be broken down by slight pressure. In the latter instance, the lumps during the processing should be spread out in a glass petri dish and broken down with a spatula, using slight pressure but no grinding action. The contents may then be returned to the screen with a wash bottle. In this way a great amount of time can be saved and accurate end points and readings obtained.

It was found that certain pigments, such as white lead and lithopone, very often show a cementing together of particles that may be due to the presence of water-soluble metallic salts. Although continued soaking in water would ultimately break up such aggregates, it was thought that the use of water as a wash liquid would be inadvisable. This is due to the fact that oil is used for factory grinding and a similar liquid should be used for pigments having cemented particles, when running a screen test. For such pigments, therefore, wash liquids consisting of mineral spirits, turpentine or kerosene have been recommended. Some may still prefer to use water, so results on both are given in the charts.

Again, with such pigments as Prussian blue a curious state of hard aggregate formation may be observed. While washing with water would break up such aggregates (peptization sometimes occurring), and in most instances show a residue

of less than 1 per cent, washing with kerosene or liquids in which these aggregates were not broken up would leave residues as high as 62 per cent.

In view of the widely varying results when solvents other than water are used, it is probable that no limit can be set for the percentage of residue from Prussian blue, when using liquids other than water. The use of mineral spirits will undoubtedly indicate to grinders what blues are best suited for rapid grinding in oil, but until color makers are able to wash and dry Prussian blue in such a manner as to prevent the formation of aggregates, it is probable that no standards within close limits can be set.

PHOTOMICROGRAPHS OF SCREEN RESIDUES

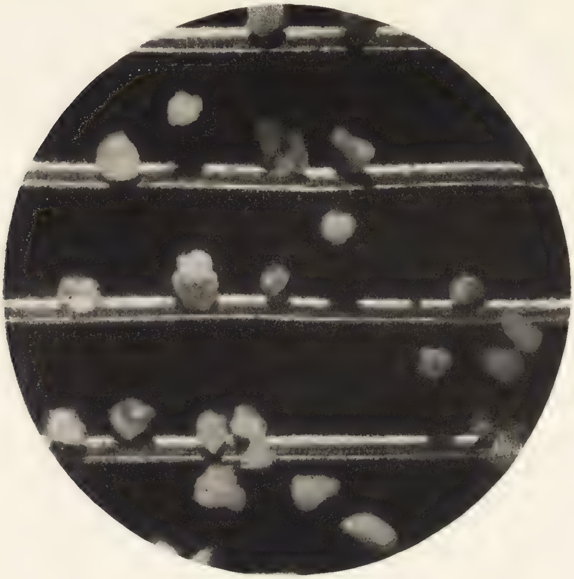

FIG. 20—Calcium Carbonate

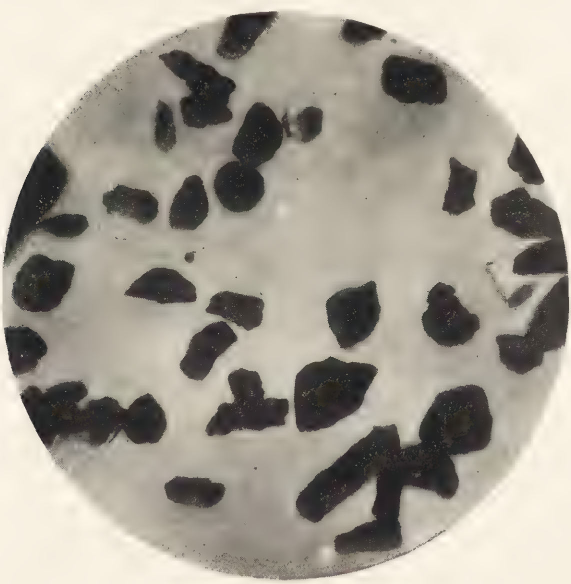

FIG. 21—Bone Black
Note Angular Hard Particles

CHAPTER V.

OIL ABSORPTION OF PIGMENTS

In mixing a pigment and a liquid a point is reached where independent of such mechanical forces as could be developed by actual grinding, the surface of each pigment particle is thoroughly wet by the liquid and the pigment mass becomes thoroughly saturated. This point represents the oil absorption property of the pigment, and is expressed by a factor termed the oil absorption factor. This factor is therefore a measure of the quantity of a given oil or liquid, required to thoroughly wet all the absolute particle surface of the pigment mass. The factor is ascertained by determining the number of cubic centimeters of liquid required to saturate 20 grams of pigment. It is then expressed as the amount required for 100 grams of pigment.

The oil absorption of a pigment is particularly important to the manufacturer who wishes to maintain a product of uniform quality and to the user who desires such a product. For instance a user of lithopone might require for a certain paint, a pigment of a certain well defined oil absorption, in order that his product would remain uniform. If a shipment of markedly higher or lower oil absorption should be sent to him, he could discover this fact by the oil absorption test, previous to storing or using the pigment.

In designing a paint the oil absorption factor is especially valuable for determining the amount of oil required to grind each pigment to paste form or the quantity of each pigment required to produce a certain desired consistency. In improving the properties of an existing paint, a consideration of the oil absorption factor is also important. Thus if it is desired to increase the consistency of a paint without increasing the percentage of pigment, high oil absorbing pigments may be used. The opposite may be accomplished by the use of low oil absorbing pigments. In using high oil absorbing opaque pigments, inert pigments of low oil absorption may be added in order to lessen the amount of oil required to suspend the other pigments. When it is desired to secure maximum opacity, regardless of other qualities, a low oil absorption opaque pigment may be used. If a glossy enamel-like finish is desired, a pigment of high oil absorption is indicated.

The amount of oil required for pigment saturation or wetting is directly proportional to the specific surface* of the pigment mass, existing at the point of saturation. As the specific surface of the mass is relative to its degree of particle sub-division or fineness, it also measures to a great extent the fineness of the pigment. The oil absorption factor being relative to the surface conditions of the pigment is independent of its chemical composition or specific gravity. The practical advantages of knowing the oil absorption factor lie in the information it gives concerning the following physical conditions of the pigment:

(a) Relative amount of surface in the pigment mass.

(b) State of sub-division of the pigment particles.

(c) Comparative specific surface of various pigments.

(d) Variation in fineness or particle sub-division of various lots of the same pigment.

TABLE XI—*Oil Absorption Factors on Some Pigments*

Pigment.	Low-Oil Absorption Type.	High-Oil Absorption Type.	Average Type.
Basic Carbonate White Lead	15	22.5	
Basic Sulfate White Lead	26	32	30
Zinc Oxide	47.6	54.1	52
Titanox	22	28	26
35% Leaded Zinc	31.3	36.5	32
Lithopone	22.75	38.5	33
Asbestine	32	50	50
Barytes	13	15	13.5
Blanc Fixe	23	36	30
China Clay	41.5	53	51
Gypsum	26	35	33.5
Silica (Crystalline)	20	28	23
Silica (Amorphous)	30	38	32
Talc	40	65	60
Whiting	28	35	32

The property of absorbing a given quantity of oil is relative to the specific surface of the pigment mass. Thus the difference in oil absorption and body imparting property shown by various pigments is due to the difference in specific surface or particle sub-division. From this it follows that the variation or differ-

* It is believed that the oil absorption of a pigment may be reduced by compacting. The small particles would then form aggregates and the specific surface would be reduced, thus reducing the oil absorption. Similarly, by effecting electrical changes in the particles to cause a coalescence or by effecting a change in the surface tension of the particles, a reduction in oil absorption might be accomplished.

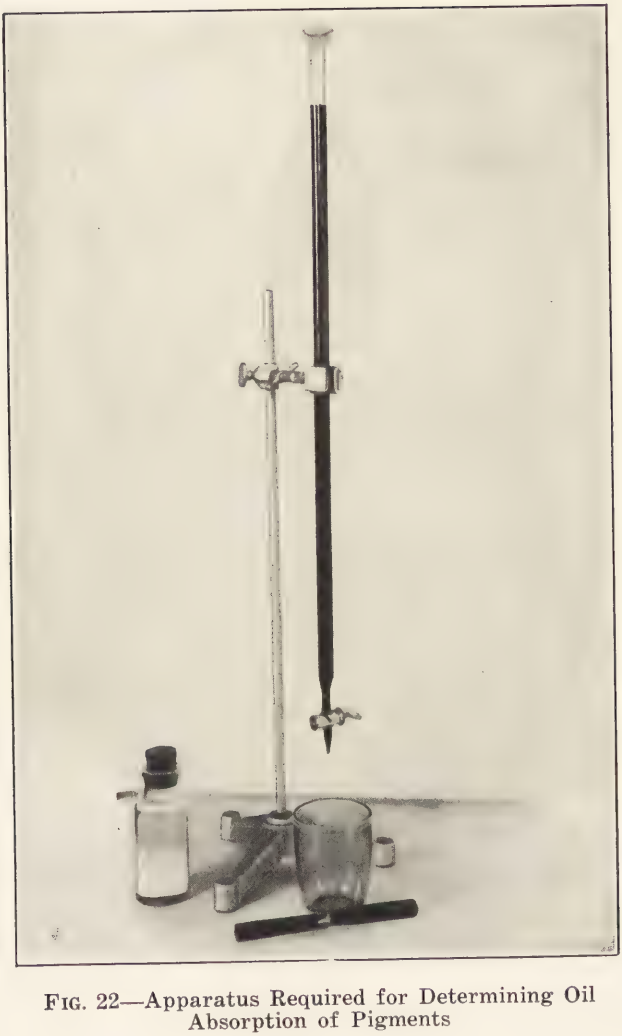

FIG. 22—Apparatus Required for Determining Oil Absorption of Pigments

ence in pigments in this respect exists up to the saturation point only. Beyond this point they all become uniform in the amount of oil required to bring the mixtures to a certain consistency. This fact is important in the comparative testing of pigments in liquid paints. The following is illustrative of its application.

If a series of pigments are ground into pastes on the basis of the individual oil absorptions of each, and the same amount of thinning mixture is then added to the same weight of each dry pigment in its paste form (pigment plus oil required to saturate), the resulting mixed paints, barring thickening due to any chemical action, will be of practically the same consistency.

Considerable information is also obtained by studying the condition of the pastes at the oil absorption point. A very considerable difference will be noted in the characteristics of the pastes produced by various pigments. Some pastes will be short and tough. Others will be long, stringy and soft. Some will have a high gloss. Others will present a dull appearance. Some of the pastes will be dense, requiring heavy pressure to flatten them out. Others will be soft and easily spread. The amount of oil absorbed does not entirely control these factors. In other words, two pigments of practically the same oil absorption may yield entirely different types of pastes. For example, one may be dense and the other soft. These physical characteristics all indicate certain pigment qualities.

The oil absorption point varies with different pigments and is influenced by certain conditions. A pigment in its dry state consists of individual particles and agglomerates of particles. The particle surface and the mass particle surface combine to make the absolute surface existing in a given volume of the pigment. As the amount of oil required to saturate a certain amount of pigment is the amount required to wet the absolute particle surface, any influence which tends to change the surface content (by changing the specific surface) varies the oil absorption point. Two common influences accomplishing such change are found in the dispersion effect of certain vehicles, and the effect of mixing and grinding pressure. While these influences are always present to some degree in all paint making procedure, the basis of the oil absorption factor should be the condition of the pigment in its dry form with the elimination of these influences to as great an extent as may be possible. The oil absorption factor of all pigments is changed to

the same relative degree by the introduction of these influences to an equal extent.

Certain oils and liquids, due to surface tension phenomena or to such colloidal conditions as effect adsorption or development of great surface, tend to cause either a coalescence of the

TABLE XII

Pigment.	Raw Linseed Oil		Soya Bean Oil.		Colloidal Condition Oil	
	Oil absorption factor.	Character of paste.	Oil absorption factor.	Character of paste	Oil absorption factor.	Character of paste.
Zinc Oxide	54	Smooth. Glossy. Quite long.	53	Same as with Linseed Oil.	56.5	Glossy. Smeary. Quite rubbery.
Leaded Zinc Oxide (35%).	36.8	Soft.	35.5	Same as with Linseed Oil.	39	Quite glossy. Smeary. Rubbery. Slightly granular.
Lithopone (High Oil Absorption).	37.5	Short. Chalky. Smooth.	37	Same as with Linseed Oil.	38	Fairly glossy. Long but not tough. Slightly granular in appearance.
Lithopone (Low Oil Absorption).	25.5	Soft and Long. Fair gloss. Contains large lumps.	23.5	Same as with Linseed Oil.	26	Very soft. Runny and smeary. Good gloss. Lumpy

pigment particles into particle agglomerates or by their dispersion effect, to break down the existing agglomerates and disperse the particles into an extremely fine state of sub-division. Either of these conditions change the specific surface of the mass and accordingly change the oil absorption point. This variation in oil absorption with different oils is illustrated by the following table, which gives the oil absorption factor of several pigments in linseed oil, in soya bean oil, and in a liquid hav-

ing a relatively high colloidal viscosity but with an apparent viscosity approximately the same as the other two.

Selection of Test Liquid.—In view of the results shown in the above chart it is important that the oil used for determining the oil absorption factor be one that will have the minimum effects in causing either a dispersion or coalescence of the pigment particles. In such a vehicle the pigment tends to form a mechanical suspension or mixture only. Thus the degree of particle sub-division or agglomeration existing in the dry pigment is retained to the greatest extent. Of the common and available oils, raw linseed oil is the best suited for the purpose. With most pigments it has but little dispersing or coalescing effect. It is therefore used as the standard vehicle for determining the oil absorbing property of a pigment. If, however, it is desired to determine the oil absorption factor with certain other liquids, the results will be relative to the dispersing effect of the liquid used. In following the standard procedure a well settled Raw Linseed Oil, clear and free from foots and having an acid value of from one to three should be used. An oil of this kind is readily obtainable and easily kept. A variation in the acid value of the oil affects the oil absorption point; the amount of oil required increasing with an increase of the acid number. This difference is due either to a greater particle dispersion or to a thickening caused by the formation of soaps. It is important, therefore, that in making determinations where very accurate results or close checks are desired, that the oil used be always of the same acid value.

Effect of Moisture on Test.—The moisture contained in the pigment, between certain limits, seems to play no important part in the determination, since check results may be obtained on portions of the same sample of pigment whether aid dried, oven dried or even slightly moist. Therefore, the ordinary air dried sample of commerce is in a satisfactory condition if it does not contain sufficient moisture to cause it to mat together or cake.

The temperature of the relatively small amount of oil used during the operation is not important, because the oil is immediately cooled by coming in contact with the much larger mass of pigment. This statement is made with the assumption that the oil is of the temperature prevailing in the ordinary laboratory. When, however, the pigment is quite warm, the oil absorption is slightly decreased. This is due to the fact that the viscosity of the oil is decreased by rise in temperature and con-

sequently the thickness of the film with which it wets the particles would be decreased. However, the difference between 70° and 100° Fahrenheit, which is the average range of a laboratory, is very slight so that the temperature need not be taken into consideration except during extremes in either way.

Principles to be Observed in Test.—The principle of this test is that of effecting the wetting of all the "particle surface" or "particle agglomerate surface" of the pigment mass without the application of mixing or grinding pressure. This is accomplished by certain oil addition and stirring procedure as described herewith. In all stirring operations, care must be taken not to cause mixing of the pigment and oil by applying pressure, as this factor will tend to vary the results. All stirring and mixing should be done very carefully and lightly. A finger and wrist motion is all that should be used, allowing the forearm to rest quietly.

When the oil first comes in contact with the pigment, a corresponding amount of particle surface is wetted. The particles thus wetted then coalesce or cling together and form agglomerates or lumps of paste consisting of oil and pigment. These small lumps of paste should be kept distributed through the mass by stirring. As the absorption of oil by the mass increases these lumps will mat together, forming larger lumps or balls of paste. With further absorption of oil by the mass, these larger lumps or agglomerates of oil and pigment paste will coalesce and with most pigments will form one large ball. (With a certain few pigments this large ball is not formed; the separate smaller lumps remaining separated.) After this point is reached a small amount of dry pigment may still be left around the bottom and lower parts of the container. This pigment is wet by bringing it in contact with the free oil existing on the surface of the large ball or lumps of paste. The end point of the determination is reached when all of this dry pigment has been taken up and wet. This point is indicated by the following condition. While any dry unsaturated pigment still remains, the paste will not smear on the glass. At the point, however, where all of the pigment particles are wet, the paste becomes soft and will smear on the sides and bottom of the container.* The balls of paste may then lose their rigidity and tend to flatten out or lose their spherical form. This point, which is very sharp, occurs within narrow limits and is the end

* See Fig. 23.

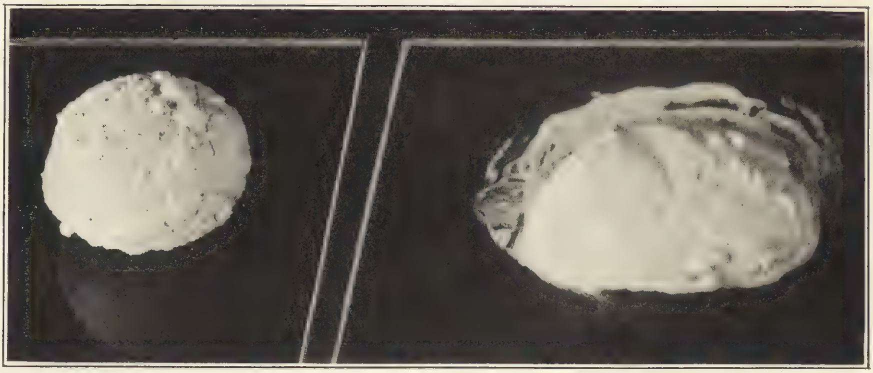

FIG. 23

Pigment Mass Just Before Point of Saturation. Mass is Spherical and Does Not Mark Glass.

Pigment Mass at Point of Saturation. Mass Loses Its Spherical Form and Smears Glass.

point. The apparatus required and method of test are given below.

Burette.—A standardized burette should preferably be used. If not standardized, the determinations should always be made by starting with the same burette filled to the zero point. In this way possible differences due to variations in the burette graduation are largely eliminated.

Container for Mixing Pigment and Oil.—For this purpose a smooth, round bottom jelly glass is very well suited. Those having dimensions of approximately 2½ inches diameter at top, and 3½ inches deep are easily obtainable. Flat bottom glasses or those having fluted sides or bottom should not be used, as the pigment and paste tend to collect in the crevices, making accurate determinations difficult.

Spatula.—A blunt end, 4 inch, stiff blade spatula should be used. If the blade is too limber, excessive stirring is required and the results are liable to vary.

Preparation of Sample.—The sample to be tested should first be placed in a suitable container (a small wide-mouth bottle is adaptable) and well shaken so as to assure the elimination of any packed particles or lumps. This is especially important if the pigment has been packed in barrels or otherwise kept in a manner that is liable to cause it to pack together. If excessively moist, the sample should then be air dried at room temperature.

Procedure.—Twenty grams of the pigment are placed in the glass. The oil is then run in from the burette, either drop by drop or with successive small additions. Either of these methods will give check results. If the drop method is used the rate of flow at the start should be about one drop per second. If the small addition method is used, quantities of ½ cc. should be added. As the absorption of the oil increases, the rate of flow or quantity of the additions is decreased. This is fully explained later. The oil is run in so as to strike the dry pigment in the center. As the oil comes in contact with the pigment, the dry pigment that has not been wet should be lifted from the outer edge and placed over the oil so as to bring all the oil surface in contact with the pigment. This is best accomplished either by lifting it up on the spatula and dumping it off on the oil, or very lightly throwing it over the oil.

When the pigment particles become wet with the oil they tend to coalesce and form small lumps of paste. These lumps should

be kept distributed throughout the mass. This is done by lightly stirring the mixture of these paste lumps and dry pigment in the manner of stirring described above, being careful not to use pressure in the mixing. If the drop method of oil addition is used this stirring should be carried on continuously with the operation of bringing the dry pigment in contact with the oil surface. If the successive addition method is used this stirring should be done after each addition. As the absorption of oil progresses these lumps of paste, by taking up more pigment and matting together, form larger lumps which when stirred around form balls. When this point is reached the rate and quantity of the oil addition should be very much decreased and only a few drops added at a time. In adding the oil at this point it should be allowed to strike on these lumps and not on the remaining dry pigment. After each oil addition these lumps are lightly stirred around so as to bring the oily surface into contact with the remaining dry pigment.

With further oil addition and stirring, these balls will with most pigments join together and form one large lump, with but little dry pigment remaining. With certain pigments, however, the lumps or balls of paste do not join together but remain separate and continue to collect more pigment. At this point, which is close to the end point, the oil is added very carefully, one or two drops at a time. With many pigments one drop is all that is necessary to establish the end point. At this stage, the oil should be allowed to strike on the surface of the lump or lumps. They should then be worked around so as to pick up more of the pigment. When all of the remaining dry pigment has been picked up and wet, the end point is reached. This is indicated as above explained by the paste lump becoming much softer and easily spread with the spatula. When stirred around it smears on the sides and bottom of the glass. This end point is very sharp and occurs within narrow limits. With most pigments only one or two drops of oil is required to change the relatively hard dry lumps which do not smear the walls of the container into a fairly soft paste which will smear when stirred around. If, when the end point is reached, the paste lumps are broken down or spread with the spatula, it will be noted that the oil is uniformly distributed throughout the mass and no dry pigment remains.

Different pigments have certain individual characteristics in absorbing oil. These must be given consideration, and it is

sometimes necessary to slightly modify the procedure in order to conform with these peculiarities. For example, some pigments absorb the oil readily and in a uniform manner, while others take up the oil slowly. The paste lumps of some are smooth and free from hard agglomerates and are easily kept uniformly mixed. Others tend to form hard lumps. With such it is difficult to keep the mass uniform. When the end point is reached with certain pigments, the paste lumps will be quite firm. Other pigments will be firm up to the end point and then suddenly become very soft; in some instances of semi-paste consistency. These differences are largely due to certain surface tension relations of the pigment and oil, a discussion of which is outside the scope of this paper. A little experience with the various pigments will enable the operator to effect such modifications as will be necessary to conform with these conditions.

Close checks can be obtained on the test made in accordance with the procedure explained above. Experienced operators rarely vary more than 0.1 cc. in check tests or in tests conducted by different operators on the same sample. For ordinary purposes a variation of 0.2 cc. is sufficiently close. A variation of more than this amount on check tests can only be considered as an error in the operation. In testing new pigments or where a close determination is desired, two or more check tests should be made. A little experience and a consideration of the following previously stated precautions is sufficient to insure accurate results:

(a) The pigment must not be moist.

(b) It should be well shaken before making the test.

(c) It should not be of a temperature lower than 70° or higher than 100° F.

(d) The oil should be well settled and of a standard acid value.

(e) The oil should not be added too fast, nor should it be added slower than is necessary.

(f) The mixture should *only* be stirred enough to keep the mass uniform and bring the pigments in contact with the oil.

(g) Excessive stirring tends to lower the result.

(h) The stirring should be done lightly and care taken not to use pressure or endeavor to mix the pigment and oil by this means.

(i) When nearing the end point, the oil should be added slowly and in small amounts (one or two drops at a time).

CHAPTER VI.

TEXTURE OF PIGMENTS

The property of many pigments to readily disperse and become finely divided when mixed with a liquid, even without grinding, is due to a quality termed "texture." This term is used to designate the structure of the pigment, and bears no relation to its fineness.

As there has been some confusion among paint manufacturers regarding the application of the terms "texture" and "fineness," the following definitions and discussion are given. A comparison of them will serve to show their proper application and import.

Fineness.—"Fine. Consisting of minute particles, grains, drops, flakes, etc." (Century Dictionary.) And its opposite characteristic, "Coarse. Coarse-grained, consisting of large particles, fibres or constituent elements." (Century Dictionary.)

From the above definitions it is apparent that the terms "coarse" and "fine" refer to the extent of the subdivision of the particles constituting a mass. They are quantity terms and are subject to the determination of degree of either property by measurement of the size of the particles.

The terms "hard" and "soft" (which are the attributes of texture) are quality terms and relate to the character of the mass or of the particles of which it consists. They are in this sense relative terms and as such are determined in degree by comparison and by such means as will indicate differences sharply.

Fineness, then, relates to the degree to which the particles have been subdivided, and texture to the character of the par-

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Texture—"Texture. By extension, the peculiar disposition of the constituent parts of any body—its make, consistency, etc.; structure in general, as the texture of rocks, the mode of aggregation of the mineral substances of which rocks are composed. It relates to the arrangement of their parts viewed on a smaller scale than that of their structure. The texture of rocks may be compact, earthy, granular, scaly, slaty, etc." (Century Dictionary.) And the attributes of texture: "Hard. Solid and firm to the touch; firm in substance and texture, so as not to be readily altered in shape, penetrated, or divided; so constituted as to resist compression, penetrating, dividing or abrading action; opposed to soft." (Century Dictionary.) "Soft. Yielding readily to pressure; easily penetrated; impressible; yielding; opposed to hard; easily susceptible of change of form." (Century Dictionary.)

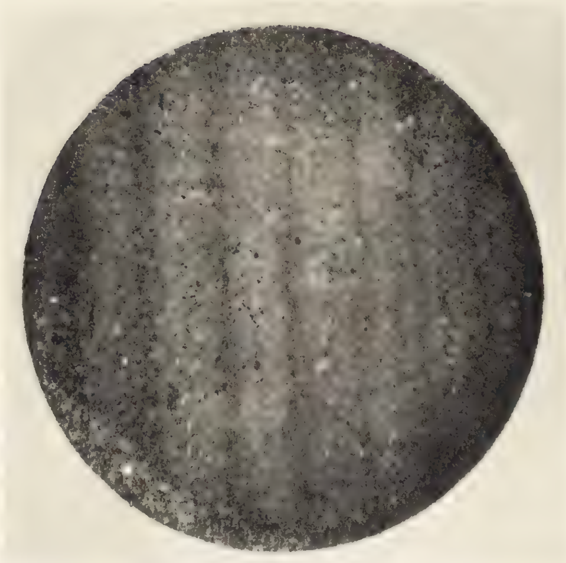

Fig. 24—Photomicrograph of paint of poor texture flowed on glass. Note coarse particles

Fig. 25—Photomicrograph of paint of good texture flowed on glass. Note fine particles

ticles, independent of their size. As applied to pigments, the important properties and the most desirable from a general paint-making standpoint are maximum fineness and soft texture, although there are certain exceptions to this, such as the use of hard pigments in wood fillers and in small amounts in certain mixed paints.

From this it will be seen that pigments of equal fineness may differ greatly in texture or of similar texture may vary in their degree of fineness. Closely related to the texture of a pigment are, ease of grinding, character of finish, settling and hardening in the package, and to some extent flowing and spreading of the paint. A pigment of soft texture disperses more readily, grinds more easily, produces a smoother finish, has less tendency to settle and harden, and makes a better flowing and spreading paint, than one of hard texture.

The test described herewith for determining the comparative texture of pigments has been widely used by certain manufacturers and found valuable as a method for setting standards and in investigation work. It is based on the extent to which pigments under certain conditions will disperse in a liquid having good dispersing properties. The liquid used is a mixture of equal parts by volume of blown linseed oil of a specific gravity of approximately .945 to .950 and pure turpentine. This mixture should be of slightly higher viscosity than raw linseed oil. If on account of age or storage in open tanks the blown oil has become heavy, a further addition of turpentine should be made so as to bring the mixture to the proper consistency. It should be strained through silk or very fine cloth before use.

Apparatus Required.—Ground or frosted glass plate about one foot square. Several clear glass plates 4″ x 4″ or 4″ x 6″. Three-inch glass muller. Artist's spatula (4″ blade). Small spatula. 50 cc. beaker. It is important that the small glass plates be thoroughly washed with soap and water, and then with alcohol so as to remove all dirt and grease from the surface. If a soft cloth is used for drying the washed glass, it should be first washed in alcohol, and dried, so as to free all loose particles of lint.

Method of Making Determination.—12 cc. of the liquid described are used with from one to two grams of pigment. The amount of any pigment used depends on its oil absorption. With high oil absorbing pigments such as zinc oxide, high oil absorption lithopone, asbestine, china clay, and similar pig-

ments, one gram is sufficient. With medium oil absorption pigments, such as low oil absorption lithopone, whiting, silica, etc., one and one-half grams are used. For pigments of low oil-absorption, such as basic carbonate or basic sulphate white lead, barytes, etc., two grams are used. As the test is only qualitative and largely comparative, a closer calculation than the above, based on oil absorption, is not important.

The pigment is mixed to a thin semi-paste on the ground glass plate with about 1 cc. of the liquid. This paste is then well rubbed out with the muller in three mulling operations for one minute each. This is done by mulling the paste continually for one minute, then scraping it up to a pile on the plate. This operation is carried out for the third time. The purpose of this mulling is to break down the particle agglomerates of the pigment and to cause each particle to become wet with the liquid. A light pressure in mulling, sufficient to thoroughly rub out the paste, is preferable to a heavy grinding pressure.

It has been found that mulling to the extent stated is sufficient to practically eliminate any variation in results, although further mulling, even with more pressure, does not materially affect the results. Between each mulling operation, a few drops of the liquid should be added in order to compensate for evaporation or thickening condition.

After the mulling is completed, thin the paste with a further amount of the liquid and transfer to the beaker. Add the balance of the liquid, and stir thoroughly. Let stand for one or two minutes to eliminate the air. Then pour the mixture on a clean glass plate, holding the plate in an almost vertical position and pouring the paint across the upper portion so that it will flow down. Place the plate in a vertical position so that the excess will drain off. It should be left in this position until the film is dry.

In this test the pigment particles of soft texture will become so finely divided that they are either colloidally dispersed or so finely dispersed as not to be visible to the eye. The harder particles which have not been finely dispersed show up. As the mixture flows down the plate, the smaller particles remain at the top in the thinner part of the film while the larger particles as well as pieces of lint and dirt flow down to the lower part of the plate and can be easily observed in this portion of the film.

Interpretation of Results.—Some pigments disperse easily and to a great extent, while others contain many small and a few

large particles which do not readily disperse. Others contain a majority of large particles. A comparison of different pigments or different lots of the same pigment will serve to show their character in this respect.

Liquids also vary in their dispersing property. Some will disperse pigments to a greater extent than others. Certain liquids may with certain pigments have the opposite effect—that of causing some pigment to agglomerate and form large, hard particles. This test may therefore be used to determine the relative dispersing properties of paint liquids. For this purpose any one pigment may be tested with several liquids in the manner described, and comparisons made.

CHAPTER VII.

VISCOSITY OF VARNISHES

Gardner-Holdt Apparatus

In making routine consistency determinations where great accuracy is not a prime consideration, the simplest and most rapid method is preferable. The widely used air-bubble test, if used with certain precautions, gives a comparative measure of consistency and is sufficiently accurate for most routine work. It is common practice, for instance, to compare a sample of varnish drawn from each individual batch with a standard sample of the same varnish which has previously been found in actual use to have the desired consistency. To make such a test, a small tube or vial is filled with the varnish and an air space is left between the surface and the cork. When the tube is inverted, the air bubble rises through the liquid at a definite rate, depending upon its consistency. The size of the bubble and the diameter of the tube are factors which also affect the rate of rise. The speed with which the bubble rises through the liquid is compared with the rate of rise in a standard sample. This test as usually made, however, is only comparative and does not give a definite numerical value that may be preserved for future reference.

The writer and his assistant, P. C. Holdt, have recently devised a simple type of apparatus that will probably be of service to the varnish superintendent and chemist. This apparatus, which is shown in the illustration below, consists of a case which holds twenty viscosity tubes filled with a series of mineral oils that will not show any change of viscosity with time. The tubes are placed in alphabetical order. The case also contains a card showing the approximate absolute viscosity of the liquid contained in each tube. Thus a varnish matching tube E would have a viscosity of 1.25 poises. It may be preferable, however, for the varnish maker always to refer to consistency E or consistency H, and so on. With the above type of apparatus available for comparison of varnishes, the use of such terms could be referred to in correspondence and be specifically understood by the operating heads of varnish departments in plants located at widely separated points.

Gardner-Holdt Viscometer
FIG. 26

In this set of viscosity tubes, the difference between any two adjacent tubes is equal to about ½ bubble. It may be found convenient to reduce the number of tubes to 10, making a difference of a whole bubble between adjacent tubes. Following are the approximate absolute viscosities of the 20-tube set:

TABLE XIII—*Approximate Absolute Viscosity in Poises at 25° C. (77° F.)*

A	0.50	F	1.40	K	2.75	P	4.00
B	0.65	G	1.65	L	3.00	Q	4.35
C	0.85	H	2.00	M	3.20	R	4.70
D	1.00	I	2.25	N	3.40	S	5.00
E	1.25	J	2.50	O	3.70	T	5.50

A similar set of viscosity tubes could be made up by anyone without reference to absolute viscosity. By blending two mineral oils, one of high and one of low viscosity, in various proportions, a set of standards covering the range of consistencies found in any manufacturer's products is readily made. The different tubes could be lettered or numbered or designated in any other convenient way.

Three factors were considered in making up the apparatus described above (1) Tubes, (2) Standard liquids, and (3) Conditions influencing the test. These factors are discussed below.

Tubes.—Various kinds of tubes are now in use for the air-bubble test. These tubes vary from the ordinary small homeopathic vial to specially made tubes, including carbon tubes with marks for fixing the size of the bubble. The proper length of such tubes is generally determined by the convenience of handling. It is important, however, that the diameters of the tubes containing the liquids to be compared are practically equal. Every tube selected for a case is first carefully calibrated and tested in comparison with a standard set of tubes which have the desired dimensions.

Since the allowable variation in the diameter of tubes is very small (not more than 0.1 millimeter), they must be accurately measured if direct measurement is resorted to in selection. The writers have been unable to secure a gauge suitable for measuring the inside diameter. It has been found, however, that if tubes having the same outside diameter as measured with a micrometer caliper were used for the bubble test with the same liquid they would be suitable for further examination and checking with liquids. In several gross of a particular type of tube examined the outside diameter of a consider-

able number was found to be 13.35 mm. ($\pm$0.1 mm.). All were 110 mm. long. This size was tentatively selected as the standard size. These are made up at a glass factory from specially selected tubing. Out of a gross, not over 20 are usually found that may be used as standards.

Standard Liquids—Since all varnishes change more or less with time, liquids which do not change should be selected as standards. Glycerin-water mixtures and sugar solutions have often been suggested as standards. In both of these there may be in certain ranges of concentration very great differences in viscosity for slight differences in composition. This result necessitates an absolute viscosity measurement for each standard liquid. There is, furthermore, in the case of sugar solutions the probability of considerable viscosity changes with time, due to changes in composition (inversion, fermentation, etc.). *The requirements of a standard viscosity liquid are, therefore, non-change with time and availability over the desired range of viscosities.* After experimentation, it has been found that satisfactory liquids may be made from lubricating oils of known types. Compounded lubricating oils, however, cannot be used, since they contain vegetable oils, and the free fatty acids contained in such oils would cause considerable change in the viscosity of the standards. On the other hand, pure mineral oils can be blended to secure any viscosity met with in varnishes, and can be kept indefinitely without change. Moreover, they have the further advantage that the viscosity of certain intermediate blends can be calculated with considerable accuracy. Hence it is only necessary to measure the viscosity of a few of the liquids in any series of blends.

Conditions.—The air-bubble test is very susceptible to temperature. Merely holding a tube of varnish in the hand a few moments is sufficient to cause a very appreciable change in the viscosity of the varnish. Precautions must therefore be taken to insure a uniform temperature in the standards and the test sample during observation. Lubricating oils and varnishes may undergo very different changes in viscosity with equal changes in temperature; hence it is necessary to use approximately the same temperature in all tests, allowing a variation of not more than 2 or 3 degrees either way. The size of the bubble slightly affects the speed with which it rises, and it should be approximately the same as that of the air bubble in the standard tubes.

Results.—In a large number of samples of all types of commercial varnishes recently examined, viscosities ranging from 0.6 to 5.5 poises at 25° C. were found when working with the Bingham plastometer.* To cover the complete range of viscosities noted above, about fifty tubes would be necessary to include differences of 0.1 poise, which is the limit of difference the air bubble test will show. It was found, however, that twenty tubes are sufficient for all practical purposes, one tube being used to represent about each one-fourth poise. For routine factory work, ten tubes showing a difference of one bubble between adjacent tubes, will probably be satisfactory. In the tubes referred to above, the viscosity of the straight oils and of five blends were determined experimentally, the absolute viscosities of the other blends being calculated. With these, however, the approximate absolute viscosity of any varnish can be very quickly noted and recorded as a definite numerical value.

In Scientific Section Circular No. 127 are given the absolute viscosities of a number of varnishes as measured in the plastometer. The absolute viscosities of the standard viscosity liquids herein described were measured in the same instrument. If the approximate estimation of absolute viscosity by this test is justifiable, the above varnishes should check with the standard tube which has been assigned the same viscosity. This has been found true. The above sets of bubble tubes are now in wide use throughout the American varnish industry.

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* See Circular No. 127.

CHAPTER VIII.

SURFACE TENSION AND INTERFACIAL TENSION OF VARNISHES AND PAINT LIQUIDS

While viscosity probably exerts a predominant influence on the working and spreading characteristics of a varnish or paint liquid, the appearance of the film after application will also depend to a certain extent upon the surface tension relations existing between the liquid film and the solid underface. Phenomena such as the tendency of oils to draw together in drops, the ease of wetting and grinding of various pigments with different oils, etc., have been conceived of as surface tension effects. The pitting of varnishes and baking japans or paints may also be at least partly due to this cause.

Surface tension as usually discussed refers to a tension or strain at the surface of a liquid in contact with air which causes the surface to act as though it were an elastic membrane. In a mass of liquid each molecule exerts an attractive force upon other molecules within a definite radius. As each molecule within the mass of the liquid is surrounded by other molecules, the attractive forces exerted upon it by surrounding molecules is equal in all directions. The molecules immediately upon the surface, however, are exposed to molecular attraction only from the interior of the mass of liquid and there is consequently a molecular pull toward the interior of the liquid. The inward molecular pull results in a tendency to contract, drawing the surface molecules inward.

While the measurement of this contractile tension at the air-liquid surface is of great theoretical interest and has numerous important applications (as for example, the determination of molecular weights, structure of compounds, arrangement of molecules in the mass, etc.) it has so far been of little assistance in solving the problems confronting the paint and varnish chemist. It does not serve to distinguish between liquids of the same class or to explain phenomena frequently observed. Difference in the density of the phases on opposite sides of the surface are so large as to obscure small differences in the tension of different liquids. Conditions existing at liquid-solid or liquid-liquid surfaces, are, however, of great importance in the present con-

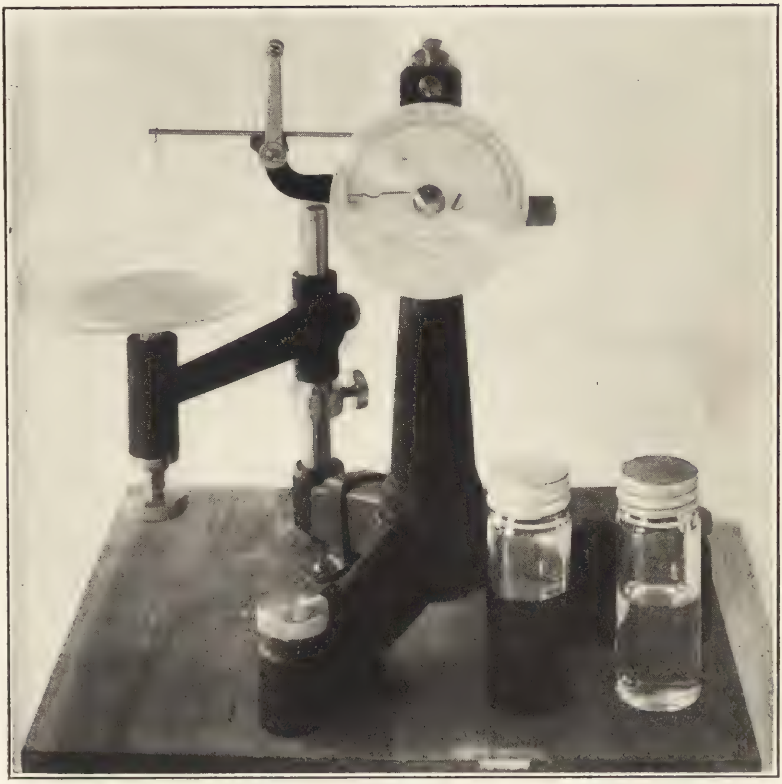


FIG. 27—This apparatus, designed by Dr. P. L. DuNouy of the Rockefeller Medical Institute, is manufactured by Central Scientific Company, Chicago, Ill. For a description of the instrument and details of operation see Bulletin No. 82, Central Scientific Company, and the Journal of General Physiology, May 20, 1910, Vol. 1, No. 5.

nection. At such a surface where the density on each side is approximately the same, differences in the intensity of the tension of different liquids against another immiscible liquid or a solid may be detected, since here the combined effects of both liquids are measured. The tension existing at other than air-liquid surfaces is usually distinguished as interfacial tension and will be so designated in this paper.

In varnishes (colloidal solutions) and paints (suspensions) where the surfaces between solid and liquid are extraordinarily great, the magnitude of the interfacial tension between the phases becomes a very important factor in determining the characteristics of the liquid.

There are, therefore, several kinds of surfaces to consider and it is desirable to ascertain whether there is any relation existing between the tensions at these surfaces in different liquids, and the characteristics of the liquid film. From a practical point of view, the most important of these various tensions is that at a liquid-solid surface. Very little is known concerning this tension, and it appears at present impossible to measure it. Relative values for the interfacial tension between immiscible liquids can be easily obtained. The absolute methods of precision which are at present available, however, apply to only one of the tensions—namely, that in the surface of the liquid against air, or its own vapor.

AIR-LIQUID TENSION

Three methods are commonly used for measuring the contractile tendency existing at the surface of a liquid in contact with air.

Capillary tube method.—Surface tension is measured by the height to which the liquid will rise in a capillary tube of known diameter. The liquid rises until the tendency of the film to contract is balanced by the weight of the column of liquid.

Drop weight method.—Surface tension is measured by the weight of a drop forming at an orifice of known diameter. The weight of the drop increases until it overcomes the surface tension of the liquid.

Air bubble method.—Surface tension is measured by the size of an air bubble forced through the liquid, the size being proportional to the surface tension of the liquid.

These methods yield accurate results but require considerable

time and manipulative skill. The apparatus illustrated and described herein is easily and quickly operated and yields results that check fairly close with the above methods. It was used for obtaining the figures given in Table XIV.

As indicated in Table XIV, surface tensions of liquids of different types, such as oils and volatile thinners, vary somewhat, but in different liquids of the same type the difference is too small to explain great differences in behavior. It also appears that liquids of different types may show the same surface tension when they would be expected to have widely varying values. The measurement of surface tension is, therefore, of little as-

TABLE XIV—*Measurement of Surface Tension Against Air by DuNouy Apparatus*

	Dynes per cm.
Oils—	
Chia raw	38.5
heated to 250° C. for 10 mins	38.5
heated to 250° C. for 20 mins	38.5
heated to 250° C. for 30 mins	38.5
heated to 250° C. for 60 mins	39.0
heated to 305° C. for 30 mins	39.0
Linseed raw	37.5
Perilla raw	39.0
Thinners—	
Turpentine	31.5
Orthodichlorbenzol	40.5
Mineral Spirits—	
No. 1	29.0
No. 2	29.0
No. 3	29.5
No. 4	29.5
No. 5	30.0
No. 6	30.5
No. 7	31.0
No. 8	31.5

sistance in studying the physical peculiarities and variations in properties so frequently encountered in paints and oils.

Since no way of measuring the tension at a liquid-solid surface is known, it is desirable that means be found for determining values which will explain differences observed in different liquids.

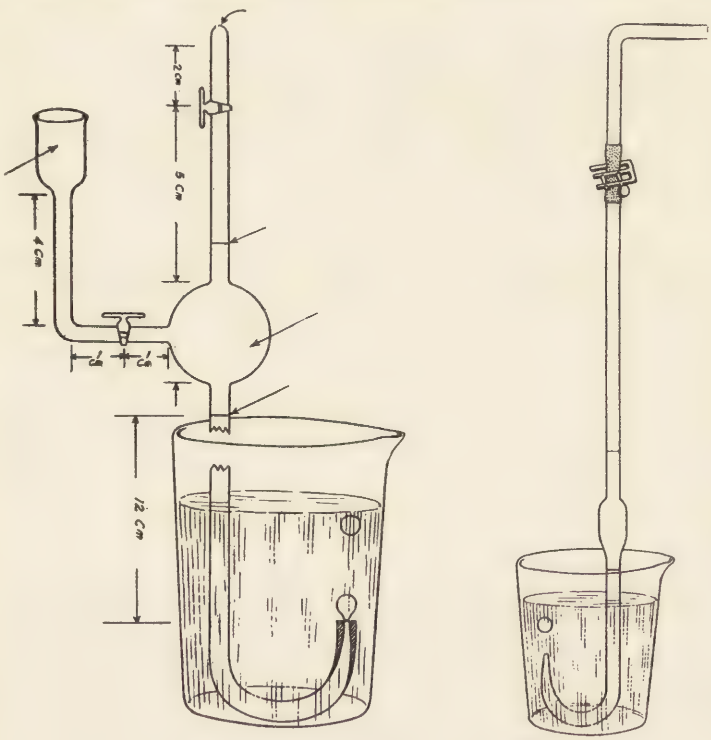
Wells and Southcombe* have observed a definite relation between the interfacial (oil-water) tension of lubricating oils and their power to wet metallic surfaces. They find that the lower this constant is, the greater will be the wetting power or "oiliness" of the oil. The ability of various oils to wet a given pigment is probably governed by the same relation. If the ten-

* Soc. Chem. Ind., pp. 51-60 T. (1920).

sion is low the oil should spread easily and be readily made to cover every facet of the pigment particles.

INTERFACIAL TENSION

Relative values for the interfacial tension between liquids were obtained by the use of the apparatus shown at B in Fig. 28. This apparatus as prepared by the writers consists of a 5 cc. pipette bent upward at the lower end and drawn to a point having an orifice of about .8 mm. It is supplied with a rubber tube and clamp to facilitate filling and to regulate the influx of air during the determination. The volume between upper and lower marks equals about 4 cc. The figures given in Table XV were obtained with this instrument. The pipette is



A B

FIG. 28—Interfacial Tension Apparatus

filled to the mark and maintained at this level by closing the clamp. The lower end is immersed in a beaker containing water or some other immiscible liquid at the desired temperature. Enough air is admitted by loosening the clamp to cause a slow

efflux of oil in a series of distinct drops from the capillary tip. As the drops break loose and rise to the surface one at a time they are counted. From 5 to 10 minutes are required for a determination.

The instrument shown at A has been designed by the writers to secure greater convenience in operation and greater accuracy, and will be used in future work. The size of the capillary to be used will depend upon the viscosity of the liquids tested. It may be advisable to have two instruments fitted with different-sized capillaries to take care of extremes of viscosity.*

If a capillary tube as shown at A is used it is essential that, in each determination, the top of the tube be perfectly clean and free from the liquid the interfacial tension of which is to be measured. If it is not kept clean the liquid in emerging will spread over the top of the tube, producing drops of non-uniform size and render the determination worthless.

The number of drops formed by a definite volume of liquid is inversely proportional to the interfacial tension. This number is influenced by both temperature and the depth of immersion of the capillary tip. Since observations are made at or near room temperature, it will be sufficient to maintain the water at the desired point, as the liquid in passing through the submerged part of the tube to the capillary tip will come to the temperature of the water. If the beaker is always filled to the same height and the instrument rests on the bottom the degree of immersion will, of course, be the same. While the results thus obtained are only relative, the values for different liquids of the same class vary greatly and the differences are such as might be expected from their properties.

In Table XV a difference in drying oils and thinning liquids not shown by the usual surface tension methods is indicated. For instance, perilla and chia oils are seen to have a much higher interfacial tension against water than has linseed oil. If the same relation holds at solid-liquid surfaces (which exists in applying the oil to a solid surface) it appears that this higher interfacial tension would account for the "crawling" of these oils. The low value found for extracted linseed indicates that the interfacial tension was reduced by the large percentage of free acid. Accordingly it was found that when different per-

* The writers have turned their design over to the A. H. Thomas Company, of Philadelphia. This firm has satisfactorily produced the apparatus in accordance with the design for $6.80.

centages of linseed oil acids were added to a linseed oil of low acid value, the interfacial tension was greatly decreased.

The addition of linseed oil to perilla oil lowers the interfacial tension of the latter against water. In the mixture of oils given the crawling effect was found to be entirely overcome. While heating for a few minutes at a high temperature appears to lower the interfacial tension, if the heat is continued longer the tension again increases. The increase in viscosity, due to prolonged heating, apparently overcomes the surface tension effects in the case of perilla oil.

TABLE XV—*Measurement of the Tension at the Liquid-Liquid Surface Against Water*

All measurements made at 20° C.

Liquids	*Number of drops*
Raw Linseed	55
Linseed extracted (acid value 22)	82
95% Linseed, 5% Linseed acids	70
90% Linseed, 10% Linseed acids	90
80% Linseed, 20% Linseed acids	225
Perilla	37
Chia	32
Perilla (heated at 230° C. for 10 minutes)	42
Perilla heated 20 mins. at 230° C	33
Perilla (heated at 260° for 2 hours)	30
Alkali refined Linseed oil	44
Acid refined Linseed oil	44
Linseed fatty acids	300
66 2/3% Linseed, 33½% Perilla	52
Varnish makers' Linseed oil heated at 500° for 2 hours	36
Perilla heated to 300° C, rapidly	35
Cold pressed Lumbang	41
AA Oil (causes pitting of japans)	33
Varnish	40
Turpentine	115
Mineral spirits	79
Against Salt Solution.	
Turpentine	135
Mineral spirits	89

Turpentine and mineral spirits which show the same surface tension exhibit a very different interfacial tension against water. This result indicates that the selection of suitable thinners for various types of paint and varnish liquids is a matter of great importance.

All solid surfaces are believed to hold an adsorbed film of moisture. Although this film may only be of molecular thickness, it may yet form a continuous layer between the solid sur-

face and the applied coat. If such is the case it is conceivable that the surface is really liquid-liquid instead of liquid-solid, and that the conditions obtaining in the measurement of the interfacial tension against water as described herein closely approximate actual working conditions. If this tension is in any way related or proportional to the tension which actually exists at a solid-liquid surface it should hold for all immiscible liquids. If a definite relation holds for the liquid to be tested against any immiscible liquid it could more justifiably be used as indicating solid-liquid tensions. When determinations were made using salt solutions the ratio between the number of drops of turpentine to mineral spirits was approximately the same as when pure water was used.

An explanation for the existence of equal surface tensions in liquids of the same kind is advanced by I. Langmuir, who refers it to the arrangement of molecules in the surface layer. He states that:

"The group molecules of organic liquids arrange themselves in such a way that their active portions are drawn inward, leaving the least active portions to form the surface layer, the active portion of the molecule being that part of the field characterized by a strong stray field (residual valence). Surface energy is thus a measure of the stray field which extends out from the surface layer of atoms. The molecules in the surface layer arrange themselves so that this stray field is a minimum.

"The surface energy of a liquid is thus not a property of the group molecules, but depends only on the least active portions of the molecules and on the manner in which they are able to arrange themselves in the surface layer. In liquid hydrocarbons of the paraffin series, the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact all these many different substances from hexane to molten paraffin have substantially the same surface energy, namely 46 to 48 ergs per square centimeter, although the molecular weights differ greatly.

"If now we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their surface energies are practically identical with those of the hydrocarbons. The reason for this is that the surface layer in both cases consists of CH_3 groups."

Accepting the above statement as true, the measurement of

the surface tension of liquids against air would yield important information in regard to substances of different molecular groupings. It will not, however, serve to differentiate in any way between liquids which have the same atoms or groups in the surface layer. While it is possible that the so-called active portions of molecules may be drawn inward at any surface, whether air-liquid, liquid-liquid, or liquid-solid, it is probable as already pointed out, that the tension in the latter cases has a very different value from the former. Different vegetable oils may therefore show the same tension against air due to the fact that they all present the same group or portion of the molecule at the air surface, but it is conceivable that in contact with another liquid or a solid (pigment) different oils may have different groups in the surface layers, particularly if the active groups possess an affinity for the surfaces with which they are in contact. We have therefore different manifestations of the same force depending upon whether we are considering the tension between the liquid surface and air or the tension between the liquid and another liquid or a solid.

CHAPTER IX.

COLOR STANDARDS FOR VARNISHES

GARDNER-HOLDT APPARATUS

Some plant managers consider it of importance to gauge the color of certain varnishes so that batches made up will closely approximate those produced at previous periods. The usual means of accomplishing this is to keep samples for comparison. It has been found, however, that varnish samples kept in glass and exposed to light, may show a substantial change in color. Another method that has been used to some extent is to make up a solution of 3 grams of potassium bichromate in 100 cc. of pure sulfuric acid, limiting the darkness of varnishes to the depth of color shown by such a solution. This solution, however, has the disadvantage of being quickly reduced, the yellow soon being replaced by a green tint. This change is sometimes noticeable on a few hours' standing. The use of such a standard would therefore require the making up of fresh solutions from day to day. A suggestion has been made that a varnish slightly lighter in color than the standard solution of bichromate referred to above, be prepared and preserved as the standard for comparison. This, however, is not always satisfactory, owing to the actual color changes which take place even in varnish and to the limitation of having only one standard rather than a number of graded colors.

The writer and P. C. Holdt have found a number of other substances that fairly match varnishes in color but which unfortunately are not permanent. For instance, iodine solutions fade in the light, metallic salt solutions such as ferric chloride are affected by the alkalinity of glass containers, ultimately throwing down precipitates and becoming lighter in color. Organic dyestuffs experimented with have proved either deficient in red or yellow, or subject to rather rapid loss of color upon standing in the light.

In the experimental work that has been conducted an attempt was made to use a set of cube rosin standards ranging from G. to WW. These were first melted and poured into perfectly dry, clear glass tubes such as are used for making the bubble viscosity test on varnishes. It was found, however, that upon

cooling the rosin would crystallize in the tubes, sometimes depositing long crystalline needles against the glass, causing an opacity which would obscure the color. Moreover the gradations of color shown by the rosin standards were entirely unsatisfactory.

As a result of a series of extended experiments, it was found that the substance known as caramel (burnt sugar), when diluted with water, produced clear solutions which exactly match the yellow amber and red ruby colors produced by various types of varnishes. In fact, the color effects produced by different strengths of aqueous solutions of caramel more closely approximate the colors of varnishes than any other substance experimented with. After considerable preliminary work, a series of

TABLE XVI

Solution No.	cc. of water.	cc. of caramel solution.
1	99.8	0.2
2	99.6	0.4
3	98.8	1.2
4	97.6	2.4
5	96.3	3.7
6	92.6	7.4
7	88.9	11.1
8	81.5	18.5
9	72.2	27.8
10	55.6	44.4
11	40.8	59.2
12	22.2	77.8

12 caramel solutions varying in color from almost water white to that of the darkest varnish, was prepared from a strong solution made by dissolving 15 grams of liquid caramel syrup in 450 cc. of water.* This concentrated solution was diluted with various proportions of water to secure the desired range of colors met with, and ranging from water white turpentine to the darkest grades of oleo-resinous varnish. The concentration of each solution is given in Table XVI. In making the dilutions, both water and caramel solutions were accurately measured from a burette.

The solutions prepared as above were sterilized to prevent

* Commercial caramel varies greatly in concentration. Several samples were purchased by the writers from various drug stores. The strength, however, may easily be adjusted, using as a standard for one sample, 3 grams of potassium bichromate dissolved in 100 cc. pure sulfuric acid (spec. grav. 1.84).

fermentation and consequent change in color. In determining the best method of sterilization, one set of samples was sterilized by heating a weighed amount of solution to boiling for a few minutes in an Erlenmeyer flask fitted with an air condenser. After boiling, the flask was again weighed and a small amount of sterile water added to replace that driven off by the heat. In making up another set of samples, one-half of one per cent of sodium benzoate was added to each solution. This sample was not boiled. A third set of solutions was made up but was not sterilized. These three sets of samples were examined at the end of three months. In the set that had not been sterilized, there were large masses of fuzzy agglomerates, indicating that considerable fermentation had taken place. In the set sterilized by heat, there were small amounts of fuzzy masses (possibly caused by some contamination in transferring the solutions to the sterilized tubes). The set of samples which had been sterilized with sodium benzoate showed absolutely no evidence of fermentation. It was decided, therefore, that this method of sterilization is the best. Later it was found advisable to use 25 per cent of alcohol in the solutions.

To test the permanency of the suggested color standards, the color strength of each solution was determined by means of the Lovibond tintometer in terms of both red and yellow. These readings were then repeated at intervals of from two to three weeks to determine whether any change was taking place. The same set of tubes was used throughout, being tightly corked after each reading. They were kept in the laboratory upon a table in the light so as to afford every opportunity for color changes. The results on a series of four readings are given in Table XVII. It will be noted that there was practically no change in the color of these standards between the first and the final readings. Any minor changes indicated were so slight as to be attributable to experimental error in observation rather than to change in the color of the solution. As a check on the results, there was made up on Oct. 12th another set of the standard solutions, by using the same lot of caramel diluted to the same concentration and sterilized by the same process. When these solutions were compared with those made up three months before, upon which the readings had been made, no change was shown.

From a strictly scientific point of view, it would be more accurate to measure color strength of varnishes in terms of

wave length and to look for color changes with the aid of a colorimeter. However, a variation in color that cannot be determined by the unaided eye is of no importance in the present connection, as approximations only are desired. Moreover, because of the high cost of accurately standardized colorimeters, such apparatus would not be available in most varnish factories. It is the writer's belief, however, that a simple form of apparatus such as is suggested in this paper, might be produced by anyone interested and quite satisfactorily serve the purpose for commercial work.

TABLE XVII—*Color Strength of Caramel Solutions (Lovibond Tintometer)*

Sample No.	Size Cell.	1st reading July 7th.		2nd reading July 15th.		3rd reading July 28th.		4th reading Aug. 22nd.	
		Yellow.	Red.	Yellow.	Red.	Yellow.	Red.	Yellow.	Red.
2	½"	2.0	.0	2.0	.0	2.0	.0	2.0	.0
3	½"	3.0	.2	3.0	.2	3.0	.2	3.0	.2
4	½"	5.0	.2	5.0	.2	5.0	.3	5.0	.2
5	½"	8.5	.2	8.5	.3	8.5	.3	8.5	.2
6	½"	16.0	.7	16.0	.7	16.0	.7	16.0	.8
7	½"	26.0	.9	26.0	1.1	26.0	1.35	26.0	1.35
8	½"	36.0	2.3	36.0	2.6	36.0	3.0	36.0	3.0
9	¼"	30.0	1.75	30.0	1.75	30.0	2.0	30.0	1.75
10	¼"	42.0	4.0	42.0	4.5	42.0	4.7	42.0	4.5
11	¼"	51.0	7.5	51.0	8.0	51.0	8.0	51.0	7.5
12	¼"	61.0	12.5	61.0	12.5	61.0	12.5	61.0	12.5

NOTE: Because of the very light color (match for turpentine) of Sample No. 1 this was not included in the readings.

In order to test the permanency of the color of varnishes, samples of exterior varnish, floor varnish, and rubbing varnish of well known commercial brands were selected. These were placed in tubes in the original undiluted condition, and also diluted with 25 per cent and with 50 per cent of pure spirits of turpentine. Five sets of tubes thus prepared were sealed airtight in viscosity bubble varnish tubes. Two sets of these sealed samples were wrapped separately in heavy paper, placed in a box so as to completely exclude all light, and so protected until the time of making a reading for color value. Two other sets were exposed to ordinary daylight in the laboratory but not to the direct rays of the sun. Readings were taken on one set of the sealed tubes kept in the dark and one set kept in the light, at the end of periods of one month. On the sets kept in the dark, no appreciable change was observed at the second reading. The

sets kept in the light, however, showed considerable change. Readings on the latter are given in Table XVIII. The change in some of these was sufficiently great to be easily detected by the eye without the use of an instrument. It is very interesting, however, to note that the change is not always a lightening of color. For instance, some samples had become very much darker in color.

TABLE XVIII—*Readings on Varnishes Exposed to Light, Showing Changes in Color Values*

Sample.	Cell.	1st reading Aug. 22, 1921.		2nd reading Sept. 13, 1921.		3rd reading Oct. 11, 1921.	
		Yellow.	Red.	Yellow.	Red.	Yellow.	Red.
Exterior Varnish	½″	42	1.1	36	1.3	33	1.3
Exterior Varnish 25% Turp.	½″	32	0.8	30	0.5	28	0.5
Exterior Varnish 50% Turp.	½″	28	0.5	23	0.5	21	0.4
Floor Varnish	½″	65	3.5	62	3.5	61	3.0
Floor Varn.+25% Turp	½″	52	1.1	50	1.3	45	1.1
Floor Varn.+50% Turp	½″	36	0.1	34	0.1	32	00.1
Rubbing Varnish	¼″	42	5.6	43	6.2	46	6.2
Rubbing Varn. 25% Turp	¼″	31	4.3	36	4.2	38	4.0
Rubbing Varn. 50% Turp	½″	42	5.0	48	6.0	50	6.0

The same combination of glasses was used in successive readings to determine whether there had been any change in color. This procedure is necessary because the combined thickness of the glasses affects the reading. For instance, a sample may match glasses 16 + 14 + 8 but be lighter than a combination of glasses 16 + 14 + 6 + 2. In the second and third readings, the same combinations of glasses as were found to match the sample in the first readings were tried. Changes were then made until the glasses matched the samples. In Tables XVII and XVIII only total readings are given.

In considering the set of 12 solutions reported on in Table XVI, it was found possible to omit samples 3 and 5. This left a series of 10 standards. Standard No. 1 is the equivalent to "Standard" for turpentine, in accordance with the Interdepartmental specifications of the U. S. Government for this material. Standard No. 9 in this new set is the equivalent of the bichromate solution used as a standard for gauging varnishes in accordance with the Interdepartmental specifications for spar varnish.

These 10 new standards, made up as outlined above and now containing 25 per cent alcohol to further guard against fermentation are sealed in glass tubes with rubber corks and shellac tops. These are placed in a special carrying case similar to that used for the bubble viscosity test standards. The upper part of the case bears a label giving the color strength in red

and yellow of each sample* in accordance with Table XIX shown below.

TABLE XIX

Solution No.	cc. of Water	cc. of Caramel Solution[1]	Size of Cell	Combination of Glasses in Lovibond Tintometer to match sample	
				Yellow	Red
1	99.8	0.2	½″		
2	99.6	0.4	½″	2.0	0.0
3	97.6	2.4	½″	5.0	0.2
4	92.6	7.4	½″	16.0	0.8
5	88.9	11.1	½″	16+10=26	1.35
6	81.5	18.5	½″	16+14+6=36	3.0
7	72.2	27.8	¼″	16+14=30	1.75
8	55.6	44.4	¼″	16+14+12=42	4.5
9	40.8	59.2	¼″	16+14+12+9=51	7.5
10	22.2	77.8	¼″	16+14+12+10+9=61	12.5

[1] Solution made of 15 grams commercial caramel syrup in 450 cc. water.

No. 1 equivalent to limit of color for turpentine, U. S. Interdepartmental Comm. on Paint Specifications, Recommended Standards for Turpentine.

No. 9 equivalent to limit of color for Spar Varnish, U. S. Interdepartmental Comm. on Paint Specifications, Recommended Standards for Spar Varnish: 3 grams potassium bichromate to 100 cc. Sulphuric Acid (Sp. Gr. 1.84).

* Although the above sets of standards may readily be made by the factory manager for his own use, the writer will be glad to furnish sets with carrying cases at cost.

CHAPTER X.

A COLOR CHANGE CABINET

For Determining the Discoloration of Interior Whites.—The cabinet shown in the illustration was designed for use in testing the "yellowing" of interior paints and enamels. It is made of galvanized iron with a double walled air space in the center. The sides and tops are provided with air ducts and holes for thermometric readings. At the bottom of each chamber, a shallow pan containing several sheets of blotting paper is placed. An ounce and a half of water is added to each pan and readily absorbed by the paper. This amount is usually sufficient to provide high humidity of the atmosphere in the white chamber for a period of 12 hours and in the dark chamber for 30 hours. The entire inner surface of one chamber is coated with flat black and the other chamber with flat white. The white chamber is furnished with electrical connections and a 75-watt blue Daylo Mazda lamp which simulates ordinary noon daylight. A 10-foot length of insulated wire is provided for plugging into any convenient electric light socket. When the lamp is lighted, the temperature in the white chamber will run from 48° C. (118° F.) to 56° C. (132° F.), at various points, whereas the black chamber will show approximately 28° C. (82° F.).

Application of Black Cabinet.—A series of metal, wood or other types of slats are coated with white paint, dried, and then exposed in the black cabinet. The warm, humid atmosphere will quickly develop differences in the colors. In two days' time a loss of reflection of about 6 per cent has been noticed in one type of paint, due to yellowing of the oil content. Marked differences in such a short period have also been noticed in various types of marketed industrial paints and enamels. In a longer period much more discernible results may be noticed. It is believed that these results may be comparable to what would occur to paints in a very much longer time when exposed on factory walls.

The addition of a small amount (5 per cent) of ammonia water to the water used in the pan in this cabinet will greatly accelerate the yellowing of the paints.

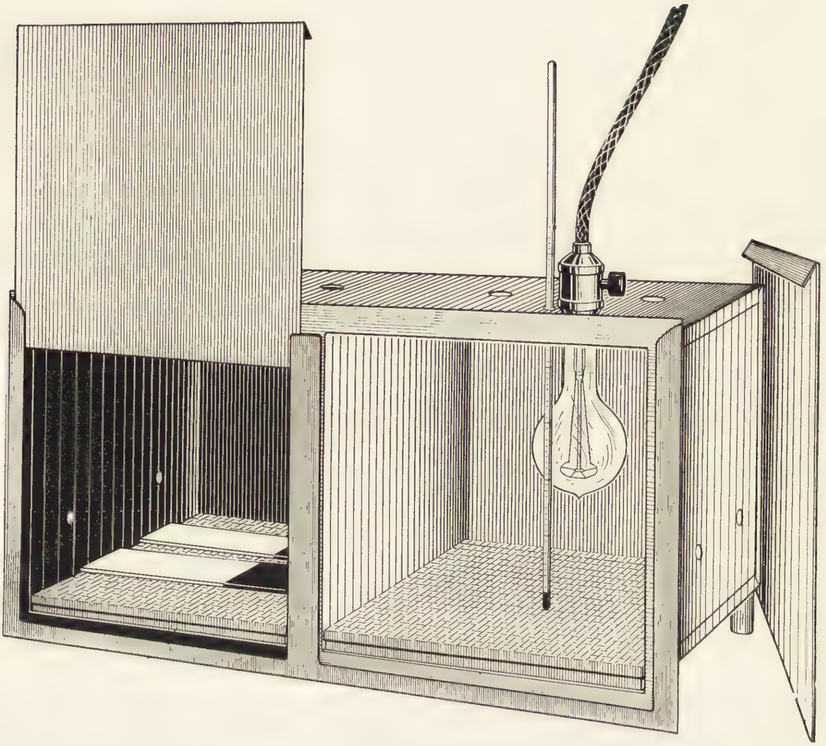


Fig. 29

Dark Chamber Light Chamber
Gardner Color Change Cabinet

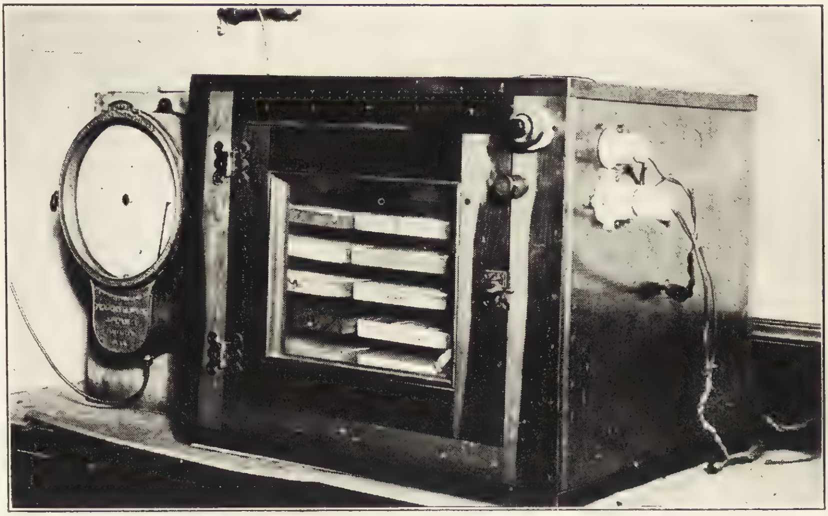


FIG. 30—Gardner Electrically Controlled Moist Cabinet With Recording Gauges

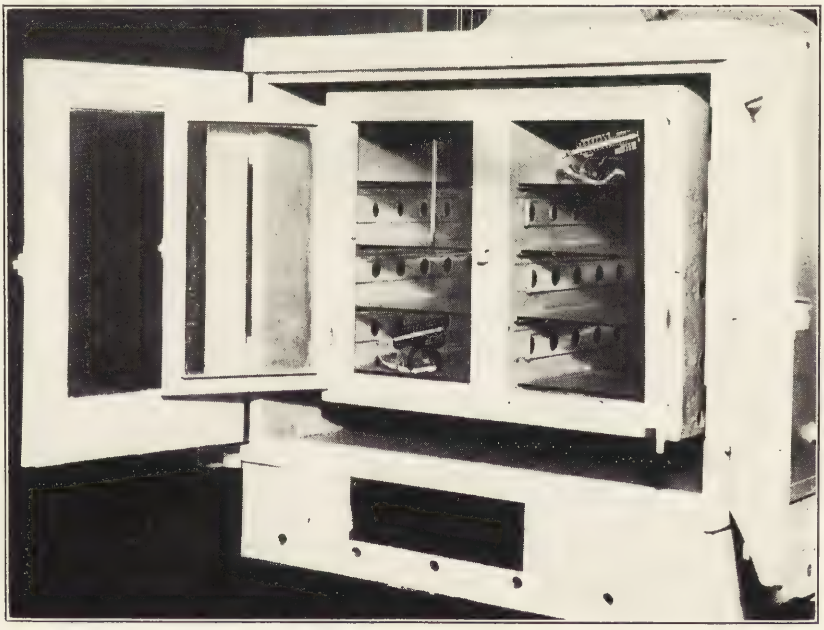


FIG. 31—Gardner Ventilated Moist Cabinet

Application of White Cabinet.—Paints containing pigments that are easily fogged by strong sunlight may, after proper exposure to the bombardment of transmitted and reflected light rays, be affected to some extent in the white cabinet. The paints may be applied to panels and exposed in the cabinet, or the pigment under examination can be rubbed up with a normal quantity of the liquid in which it is to be used in paint. This may then be spread upon a panel and dried. Half of the surface may then be covered with black paper. Daily examination of the panels, until a difference is noted in the covered and uncovered portions, will be instructive. Similar tests may be made on organic colors that may be easily affected by light. It should be remembered, however, that the light from a Daylo Mazda lamp is extremely mild as compared to that from an ultra-violet arc; the latter giving effects in a few minutes that are not obtainable over a long period of time by other means. The white cabinet described above may, therefore, be of but little use when a quick test for fogging is desired. The writer is, however, endeavoring to arrange a cabinet with an extra compartment provided with an iron arc rich in ultra-violet rays.

Corrosion.—Either cabinet may find some application in determining the comparative corrosion resistance of metal panels. The temperature and high humidity should give noticeable results. Similarly it may be used for determining the rust-inhibitive properties of pigments. In the latter case the pigment is mixed to a thin paste with water and applied to a small area on a brightly polished steel surface. After exposure for forty-eight hours, the test plates are removed, the pigment washed off, and the area formerly covered by the pigment examined for signs of rust or etching.

Drying of Paints and Varnishes.—The drying of paints or varnishes in moist atmospheres at definite temperatures might be determined in either cabinet, under light or dark conditions. Other applications of the cabinet may be developed. It is easily constructed and can be made by any local tinsmith. Those who do not care to have them made locally can secure them from the writer at cost.

Cabinets in which the drying of paints and varnishes may be determined under set conditions of temperature and humidity have also been designed by the writer. These are shown below. They have been described in early publications of the Scientific Section.

CHAPTER XI.

USE OF THE MICROSCOPE IN EXAMINING DRIED PAINT AND VARNISH FILMS

The microscope has become practically a standard instrument in the equipment of paint and varnish laboratories for the examination of paint pigments. It is believed that its usefulness may be greatly extended by applying it for the examination of all finished paints, enamels or varnishes when spread out and dried. The elasticity, hardness, porosity, resistance to water, and other physical properties are indicated by examination at low magnifications. Some of the illustrations shown herewith, which are fully described in the titles, demonstrate this point.

When new materials are proposed as constituents of existing formulae, test batches may be made, brushed out, dried and examined for the characteristics noted above.

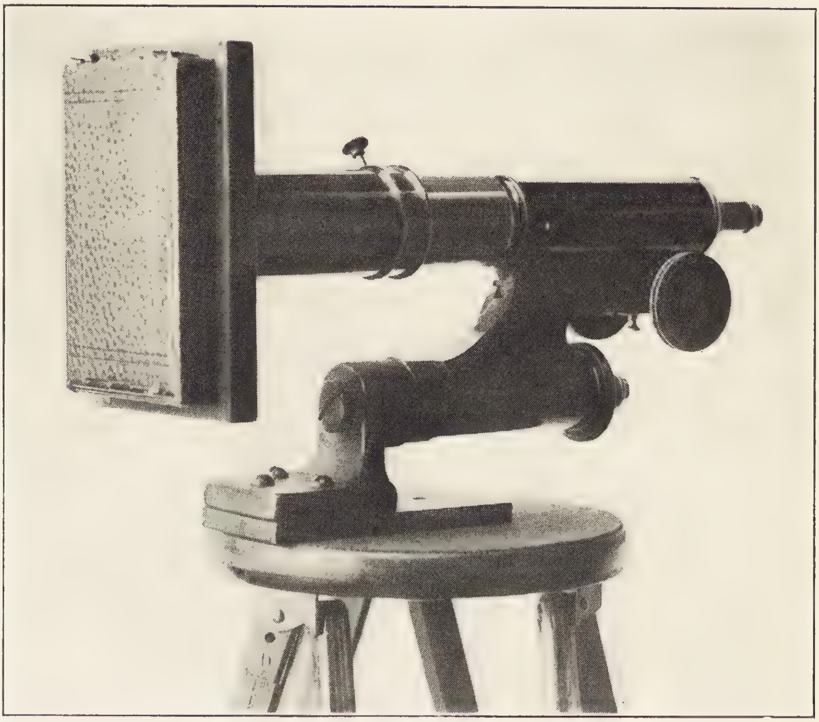


FIG. 32
Gardner Photomicrographic Camera for Use in Field.

FIG. 33—Photomicrograph of surface of an interior rubbing varnish. Surface was scratched with a needle. Note clean cut effect due to hard film.

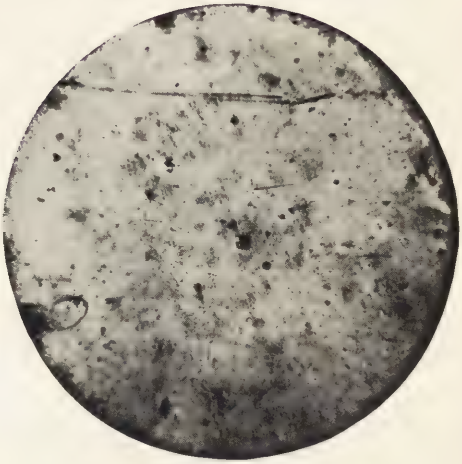


FIG. 35—Photomicrograph of surface of an exterior spar varnish. White, Cloudy effect caused by immersion in cold water. Water has not abraded or injured film but has possibly formed an emulsion with the outer layer.

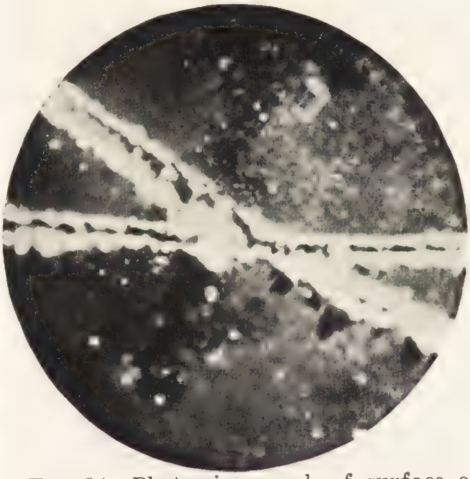


FIG. 34—Photomicrograph of surface of exterior spar varnish. Surface was scratched with a needle. Elastic and comparatively soft nature of film indicated. Also note dark spots due to particles of polymerized oil that have become insoluble. These particles are often the cause of a "sandy" surface.

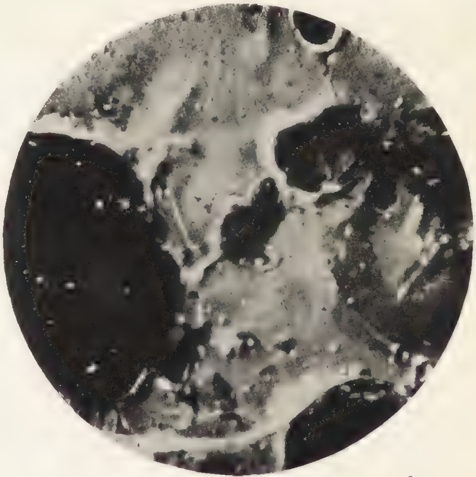


FIG. 36—Photomicrograph of surface of an exterior oil coating showing effect of boiling water which has caused the film to "creep" or pull away from the surface, leaving crater-like bare spots. To the naked eye a white and rough surface is indicated.

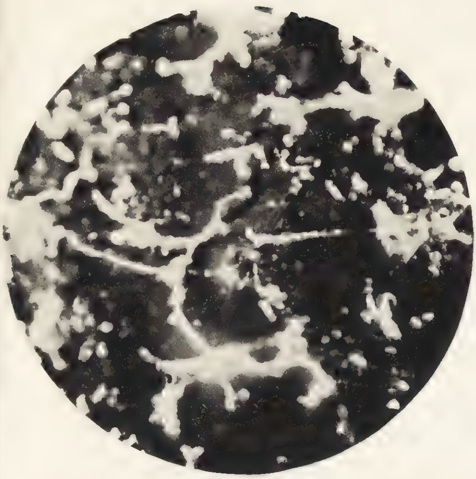


FIG. 37—Photomicrograph of surface of an oil coating that has shown peculiar crinkling, probably due to surface tension effects.

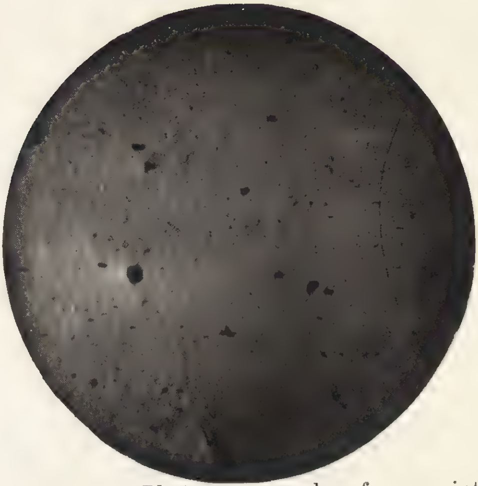


FIG. 39—Photomicrograph of a paint coating. Thinner used in the paint was too volatile. Upon evaporation from film, it caused formation of small craters.

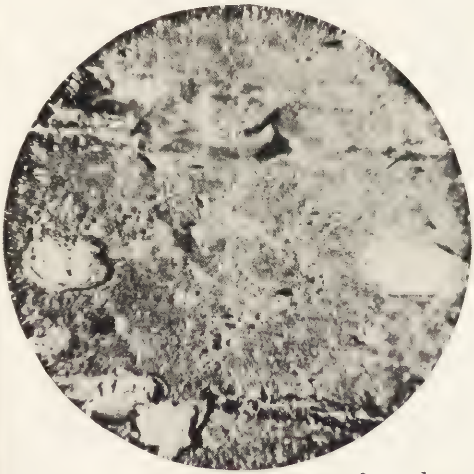


FIG. 38—Photomicrograph of a drawn metal article. Note abraded effect of metal. Rapid corrosion would follow unless protected with paint or varnish.

FIG. 40—Photomicrograph of a paint coating. Paint was not properly ground in mill. Note rough, granular surface of unground pigment particles.

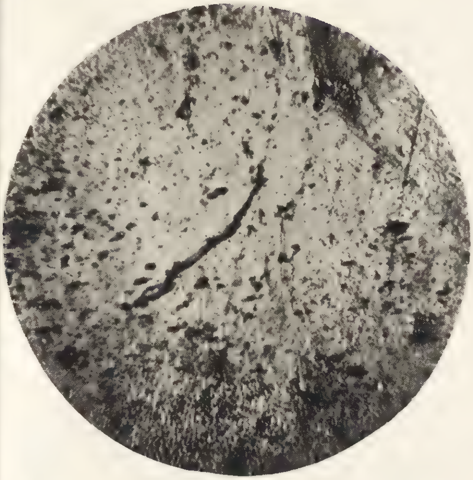


FIG. 41—Photomicrograph of a wall coating. Drying in a dusty room caused adherence of dust particles. These gave surface a darkened appearance.

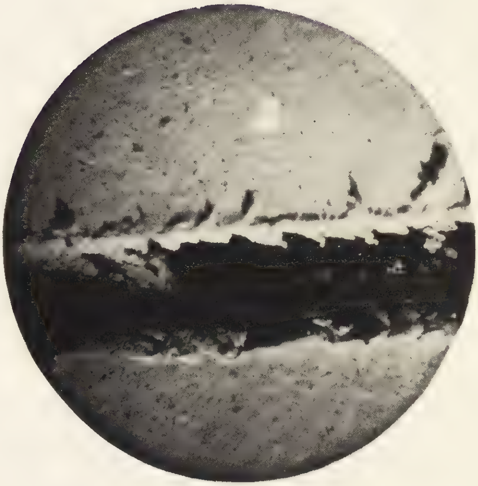


FIG. 42—Photomicrograph of an experimental flat coating. Paint contained too much volatile matter. Scratch made with a metal point shows dry nature of film.

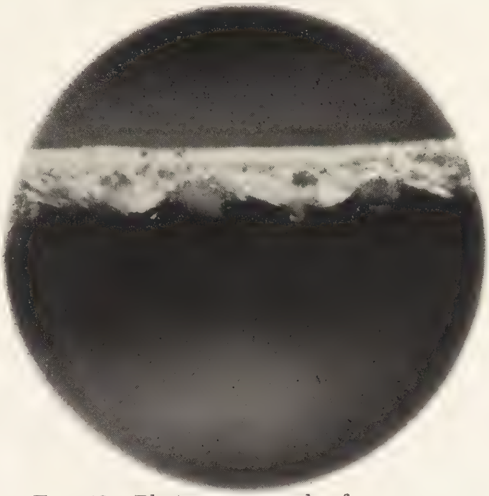


FIG. 43—Photomicrograph of a cross-section of an enamel coating on oilcloth. Note warp and filling threads of cotton fabric, filled surface, and smooth outer white enamel film.

CHAPTER XII.

SUGGESTIONS FOR MAKING
EXPOSURE TESTS ON PAINTS AND VARNISHES

(EXPOSURE TESTS ON PAINTS)

(a) Select a soft wood such as white pine or poplar, unless it is desired to get special information as to the durability of paints on such woods as red cedar, yellow pine, or cypress. The latter woods are used where the penetrating properties of special primers are being studied.

(b) The panels used in previous tests made on a large scale were constructed to be $36'' \times 18''$ of three widths of siding, with a weather strip at the top. They were braced at the back. (See reports on the Atlantic City and Pittsburgh tests in early circulars of Scientific Section.)

(c) When space for such panels is not available, boards $15'' \times 6'' \times 1''$ of dressed lumber are used. Allow the finished panels at least a week's exposure to sun and weather previous to painting. Then air-dry in laboratory for a week, if they are to be painted inside.

(d) Always make tests in duplicate.

(e) If panels are to be painted inside on account of bad weather, allow each coat to dry indoors for 24 hours and then place out-of-doors for a period of at least three days' drying between coats. If possible, allow 10 days time between the coats for drying. The durability of any paint depends largely upon the period allowed for the drying of the successive coats.

(f) If a white paint of a new formula is being tested, apply the paint in light tints as well as in white. Chalking of the white paint is not easily noticed. Chalking of light tints of the same paint will often be noticed by the flooding of the chalked white pigment, which is often termed "fading." Rich cream, pea green, and sky blue tints are suggested.

(g) If possible, make exposures under two or more climatic conditions in various parts of the country.

(h) Expose panels facing south. If panels are inclined at an angle of 45° to the vertical, they will show the most rapid results.

(i) For metal paints, the selection of sand-blasted panels is preferred, since test panels free of loose mill scale are not easily

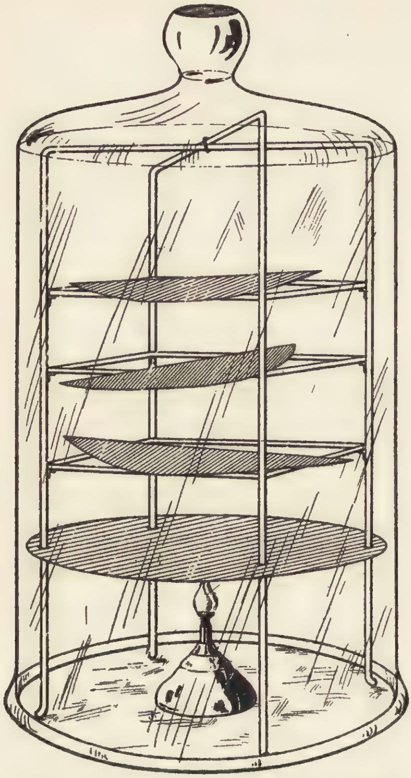


FIG. 44—Apparatus for determining gas resistance of varnish. See Interdepartmental Specifications, back of volume.

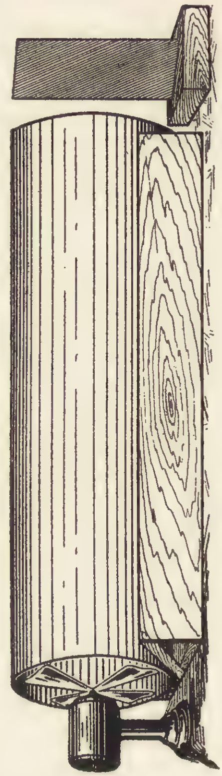


FIG. 45—Apparatus for determining draft resistance of varnish. See Interdepartmental Specifications, back of volume.

FIG. 46—Old panel exposure tests back of laboratory.

obtainable. Cleaning of the surface of metal panels with benzol to remove grease is advisable previous to test. Metal panels 15″ × 6″ and of 18 to 22 gauge are of sufficient size for a test if made in duplicate or triplicate. Where space is available, panels 24″ × 36″ are preferable.

(j) Examine the tests at least every six months and record the results on a blank form, in accordance with the standards of the American Society for Testing Materials, as given below.

A. S. T. M. Method for Reporting Condition of Exposure Tests.—It is important that uniform, precise and relatively accurate methods for describing or measuring the character and amount of disintegration of paint coats be adopted. Unless such standards are evolved, reports made on the wearing values of paints by different investigators or observers cannot be intelligently or accurately compared.

In considering the adoption of definitions for terms generally used in reporting condition of painted surfaces, descriptive words now in common use have been adhered to. In addition, an effort has been made to assign numerical values to these descriptive terms with the idea of ultimately working out some scheme whereby paint tests may be given a definite rating. A great deal of study is still required in order to assign values to the descriptive terms, so that the final rating may not only be an accurate one, but that it may really represent some well-balanced and understandable relative measure of service value.

Checking.—Checking describes slight breaks in the paint coat which do not extend through to the surface painted. This is reported and rated as:

Absent	10.0
Very slight	9.9 to 8.0
Slight	7.9 to 6.0
Considerable	5.9 to 4.0
Bad	3.9 to 2.0
Very Bad	1.9 to 0.0

Alligatoring.—Alligatoring describes an aggravated form of checking. The breaks in the paint coat are wider than in checking and usually extend almost through to the surface painted. While the condition is seldom observed, it is advisable to include the term "Alligatoring" in the list of definitions. This condition is reported and rated same as for "checking."

Cracking.—Cracking describes a break which extends down to the surface painted. It may be a break which immediately

extends down to the surface painted or it may be the development of what was first checking or alligatoring.

On wood, cracking is usually parallel with the grain, although sometimes it is at right angles to the grain. This condition is reported and rated same as for "checking."

Flaking.—Flaking describes the falling away of small pieces of the paint coat. This type of disintegration is generally the result of checking which gradually develops into cracking, ending in the crumbling of the paint coat. This condition is reported and rated same as for "checking."

Scaling.—Scaling describes the breaking away of pieces of paint of considerable size. This condition is generally the result of long cracks, on wood, usually parallel with the grain. This condition is reported and rated same as for "checking."

Blistering.—Blistering describes a condition where the paint coat is detached and raised from the surface over which it is applied, due to the formation of gases beneath the coating, influenced generally by moisture behind the coating.

The breaking of the blister results in peeling of the paint coat.

Peeling.—Peeling describes the pulling away or falling away of large pieces of the paint coat from the surface to which it was applied.

Peeling of paint is not the result of natural wear, but is due to improper application or to adverse conditions at the time of painting, such as moisture behind the paint coat or a faulty application of the priming coat.

Gloss.—Although much depends upon the nature of the coat, it is not advisable to report condition of gloss after a paint has weathered for more than a year. The gloss which a paint had shortly after its application disappears in proportion to the chalking of the paint, and while it is possible to restore a gloss to a surface in some cases, by rubbing, the gloss restored is the result of abnormal treatment. Gloss may be reported as:

Very Good	10
Good	9.9 to 8.0
Considerable	7.9 to 6.0
Slight	5.9 to 4.0
Very Slight	3.9 to 2.0
Absent	1.9 to 0.0

Chalking.—Chalking describes the reduction of the outer surface of the paint coat to a powdery substance, which may be removed by rubbing the coating with the dry finger, or a piece

of soft, dark colored cloth, preferably black velvet. This condition is reported as follows:

Absent	Considerable
Very Slight	Heavy
Slight	Very Heavy

It is a difficult matter to assign uniformly satisfactory ratings to the qualifying terms and, therefore, while the report should include the item of "chalking,' it is considered advisable to eliminate ratings.

Hiding.—Hiding is judged entirely by the degree of concealment of the surface painted. This property is frequently referred to as "covering" which more correctly applies to the area over which a given amount of paint will spread. Hiding is reported as follows:

Very Good	10
Good	9.9 to 8.0
Fair	7.9 to 6.0
Poor	5.9 to 4.0
Very Poor	3.9 to 2.0
None	1.9 to 0.0

Color.—Paints are divided into three classes, whites, tints, and colors. The degree of whiteness determines the character of report for the first class. Two things generally influence color; first, the hiding power, and second, chalking. Invariably a paint that chalks presents a better color than one that does not. The impression gained through the eye serves as the basis for report regarding the color of paint. The original appearance need not be considered. While all colors show a natural fading out, some retain a pleasing tone while others appear distinctly muddy or lack the brilliance shown when first applied. The terms used for reporting color are:

Very Good	Poor
Good	Very Poor
Medium	

It is not considered advisable to assign ratings to the descriptive terms.

General Appearance.—The general appearance of painted surfaces can really be determined only by viewing them from a distance of twenty or thirty feet, with the idea of forming an opinion as to whether the appearance is good, which will be influenced by such conditions as cracking, scaling, chalking, and other conditions usually found in paint wear.

Exposure Tests on Varnishes.—For making exposure tests on varnishes, the following suggestions will be of value.

(a) Use a series of unfilled panels of dressed maple wood 15″ x 6″ x ⅞″. Apply three coats of the varnish to be tested, allowing three days for the drying of each coat. Always test at the same time a varnish of similar type, the durability of which has previously been determined by exposure.

(b) After the first coat has been applied and dried indoors for three days, it should be lightly sandpapered with No. 00 sandpaper before applying the second coat. The second and third coats, however, should be applied without sandpapering or rubbing. The backs and edges of the panels should be varnished with three coats of the sample but for these surfaces the details of application need not be adhered to, as the effects of exposure on these surfaces are not considered.

(c) Three days after application of the third coat, the panels should be exposed out-of-doors, 45° to the vertical, facing south. Inspection of the varnished panels should be made every two weeks, and the following reported. I. When first cracks appear. II. When cracks appear on every square inch of surface. III. When varnish may be said to have perished. Differentiate between surface cracking and cracks that go clear to wood. Make inspection based on careful visual examination, not microscopic examination. If panels are in a smoky community, wash lightly with water and sponge previous to examination.

(d) In the same manner, panels that have been coated with black, red, yellow, green or similar colored paints may be used for exposure of the varnish. For instance some varnishes used on agricultural implements that are painted in gaudy colors, may wear well over certain colors but not over others. Information of value may be secured in this manner.

(e) It is also well to make a series of exposures similar to the above, using tin plate in place of wood. Considerable data of interest will be thus obtained.

CHAPTER XIII.

TESTING COLORS FOR TONE AND STRENGTH

Generally speaking pigment colors are bought on physical tests rather than chemical analysis. While it is true that the knowledge of the exact chemical composition of a color may be desirable for certain uses nevertheless the value and suitability of colors for most purposes can be quickly determined by physical tests for overtone and strength, and while making these tests, the relative oil absorption, texture, etc., can be noted. Suggestion made by A. F. Brown are included below.

In testing for overtone and strength it is absolutely essential that certain fundamental principles be observed, otherwise, the tests of two given samples will be misleading. The common practice of weighing roughly a given amount of color, then adding a certain number of drops of oil and rubbing an indefinite length of time with a spatula is apt to result in erroneous conclusions. Not only is it necessary that the dry color be accurately weighed, but the vehicle should also be weighed. Two colors ground in different vehicles should never be compared, as different vehicles produce different effects with the same color. Sufficient vehicle should always be used so that when the color has been rubbed and applied to a strip of glass, or tin, the surface has a high gloss. In comparing the overtones of two colors, if it so happens that one sample has higher oil absorption than the other, sufficient additional oil should be used with the color having the higher oil absorption to produce a paste of about the same consistency, otherwise the comparison will be misleading.

The amount of dry color used in making tests depends upon the type of color and the oil absorption. For C. P. Blues and C. P. Para and Toluidine Toners 0.5 grams of color is sufficient, while for C. P. Chrome Greens, C. P. Chrome Yellows, C. P. Oranges and all reduced colors, one gram of dry color is not too much. The proper amount of vehicle is dependent upon the oil absorption and the type of vehicle used. Experience has shown that where colors are to be used for certain purposes such as enamels, tests are more comparable to factory practice if rubbed in a viscous non-volatile medium such as a polymerized linseed oil

about the consistency of 00 litho varnish, instead of raw or refined linseed oil. In a general way the proper proportion of dry color to vehicle is as follows:

TABLE XX

	Raw Linseed Oil		Polymerized Linseed Oil (00 litho varnish)	
	Gram color	Gram oil	Gram color	Gram oil
C.P. Iron Blues	.5	.5	.5	.6
C.P. Para Toner	.5	.5	.5	.6
C.P. Toluidine Toner	.5	.5	.5	.6
C.P. Chrome Green Light	1.0	.3	1.0	.35
C.P. Chrome Green Medium	1.0	.35	1.0	.40
C.P. Chrome Green Deep	1.0	.40	1.0	.50
C.P. Chrome Yellow	1.0	.40	1.0	.40
C.P. Chrome Orange	1.0	.40	1.0	.40
Reduced Chrome Greens	1.0	.35	1.0	.40

In weighing, it is desirable to use balanced watch glasses counterbalancing the sample against the standard with which it is to be compared; the dry colors being first weighed and then the vehicle which is placed slightly away from the color. With a little care, no trouble will be had in transferring the mass to the rubbing slab. Some operators prefer to add the oil from a burette, each drop of raw oil being assigned a definite weight. Bodied oils, however, could not be accurately weighed by such a method.

The materials should be very carefully transferred to the rubbing slab. Plate glass about 24″ x 24″ that has been lightly sandblasted (such as can now be obtained from any chemical glassware supply house) serves very well as a rubbing slab, and a glass muller with a 2½″ face is about the right size. The color and vehicle are first mixed with a spatula until there are no dry particles of color, then the resultant paste rubbed with the glass muller a definite number of times, care being taken to exert the same pressure on both samples so that the relative development will be exactly the same.

Thc number of times a color should be rubbed depends upon the type of color and the actual factory practice as regards development. In some factories colors are well ground, but in many ostensibly efficient plants it is surprising how little attention is given to securing the maximum money value by com-

plete development. In a general way the number of "rubs" necessary to secure development equivalent to average factory practice is as follows:

C. P. Iron Blues	100 times
C. P. Para Toners	100 times
C. P. Toluidine Toners	100 times
C. P. Chrome Greens	50 times
C. P. Chrome Yellows	50 times
Reduced Colors, all kinds	25 times

In rubbing, the muller should traverse a space about three inches wide and twelve inches long, the operator pushing the muller up one side and down the other side of this strip so that all the color particles receive the same amount of attrition every rub. By one rub is meant one complete movement up and down. In testing a color which requires twenty-five rubs the color should be scraped up after fifteen rubs and then rubbed another ten times; when testing a color requiring more than twenty-five rubs the color should be scraped up with a spatula after each twenty-five rubs. After the rubbing is completed the comparison for overtone should be made by applying liberal portions of each color to glass or tin in juxtaposition. The larger daub of color the better, but in any event each daub should not be smaller than a half-dollar and they should be placed in juxtaposition, care being taken that the edges just touch but do not overlap and that there is a well defined line of demarcation. After being so placed and before comparing, a wide spatula should be lightly drawn over both at the same time to produce a color surface that will be smooth and free from ridges. In comparing for overtone, the colors should *not* be examined through the glass. For this reason strips of tin are preferable to glass as it effectively prevents this practice. If the colors are to be used for inks, this test may be made upon bond paper. Observation of the stained paper when held to the light will show whether the color is clear, bright or muddy.

For making strength tests, it is well to have a stock paste of zinc oxide in oil. Such a paste can be made by grinding 185 parts of zinc oxide and 115 parts of OO litho oil several times through a roller mill. A strength test can then be quickly made by taking a small amount of the paste color made as outlined above for comparing the overtone and adding the proper amount of zinc oxide paste.

For reduced colors a reduction of 20 to 1, *i. e.*, 20 parts zinc oxide paste to 1 part paste color, is usually sufficient but for C. P. colors a 100 to 1 reduction is necessary to get the proper idea of relative strengths. Very often two C. P. colors which apparently are about the same strength on a 20 to 1 reduction are very far apart on a 100 to 1 reduction. In making the reduction test the best way is to counterbalance 100 milligrams of the two paste colors to be tested and then add to each, two grams of the paste zinc oxide. Before removing from the counterbalanced watch glasses mix the color with the zinc oxide, using a small spatula thus minimizing the loss on transferring, then remove from watch glass to a *smooth* piece of glass and mix with a spatula until the color no longer streaks, which indicates that it is thoroughly incorporated. Never make a strength test on a rough glass and do not rub with a muller, as this develops strength that is not secured in factory practice. In the event that a 100 to 1 reduction is desired, take 500 milligrams of the first reduction, add 2 grams of zinc oxide paste and proceed as before.

If it is desired to express quantitatively the tinting strength of the color, consider the standard color as having a tinting strength of 11, and then vary the amount of the standard color until the tints are matched.

For example, let the amount of standard color for 100 strength test be 0.02 g. $(=A)$. Vary this amount in units of 5 per cent, thus 0.019 or 0.021. Let the amount taken to match a given strength $= B$, then

$$\frac{A}{B} \times 100$$

equals the tinting strength of the sample to be tested.

If the tone varies it may be difficult to make this measurement.

The comparison for overtone should be made as soon as the colors have been applied to the strip of glass or tin, otherwise "flooding" may result in one or both samples and there will be no basis for comparison.

Generally speaking it is good practice to have separate rubbing glasses for each of the four general classes of color—green, yellows, blues and reds to avoid contamination of one color with another. If one glass is used for all colors, great care must be exercised to insure absolute cleanliness. It is surprising, for instance, how little chrome green is required to off-shade a primrose yellow. Benzol 90° is probably the best liquid for cleaning the rubbing glasses.

CHAPTER XIV.

ROUTINE TESTING METHODS FOR SOME PHYSICAL PROPERTIES OF WHITE PIGMENTS SUCH AS ZINC OXIDE, LEADED ZINC AND LITHOPONE

The following routine tests for color, brightness, smoothness, tinting strength and settling are contributed by the Research Laboratory of the New Jersey Zinc Co.

Color.—Approximately 5 grams of the sample shall be thoroughly mixed with the smallest quantity of bleached linseed oil that will produce a smooth paste. This paste shall be spread on a palette of colorless plate-glass in a smooth and even layer, that will not transmit light and is at least 1 inch by 3 inches in area.

An equal amount of the standard (or each of the standards) shall be prepared in the same way, care being taken to bring the paste to the same consistency as the sample being tested. This paste shall be spread in a similar manner on the palette beside the sample, touching it, and the two compared in diffused daylight. In doing so, the palette shall be tilted so that the light will strike the surface of the pastes at different angles and the under surfaces shall also be observed through the glass.

In doubtful cases, only the sample and one standard may be spread on the palette at the same time, and their edges must touch.

To be on-grade, the sample must be as white as the standard.

Brightness.—Five grams of the sample and 1.20 grams of bleached linseed oil shall be mixed to a smooth, uniform paste. The oil used may be determined by dropping from a point which has been standardized by counting the number of drops necessary to weigh 1.20 grams. The dropping shall be at a rate not greater than 70 drops per minute. All the sample and all the oil must be thoroughly incorporated. This paste shall be spread on a palette of colorless paste-glass in a smooth and even layer that will not transmit light and is at least 1 inch by 3 inches in area.

When the nature of the pigment requires more oil than above noted, more shall be used but comparisons shall be made only between samples which have a like oil-vehicle ratio.

An equal amount of the standard shall be prepared in the same way. This paste shall be spread in a similar manner on

the palette beside the sample, touching it, and the two compared by observing in diffused daylight the two samples by looking through the glass.

In doubtful cases, only the sample and one standard may be spread on the palette at the same time, and their edges must touch.

To be on-grade, the sample must be equal to or better than the standard in brightness or brilliancy.

Smoothness and Freedom from Specks.—Approximately 5 grams of the sample shall be thoroughly mixed with the smallest quantity of bleached linseed oil that will produce a smooth paste. This paste shall be spread on a palette of colorless plate-glass in a smooth and even layer that will not transmit light and is at least 1 inch by 3 inches in area.

An equal amount of the standard shall be prepared in the same way, care being taken to bring the paste to the same consistency as the sample being tested. This paste shall be spread in a similar manner on the palette beside the sample, touching it, and the two compared in diffused daylight. In doing so, the palette shall be tilted so that the light will strike the surface of the pastes at different angles.

In doubtful cases, only the sample and one standard may be spread on the palette at the same time, and their edges must touch.

To be on-grade, the sample must contain no more granular or foreign matter than the standard. This is to be determined by the feel under the knife and the amount of noise made in rubbing down and by observation of the surfaces after the pastes have been spread on the palette.

Tinting Strength.—Five grams of the sample, 0.5 grams of ultramarine blue and 1.20 grams of bleached linseed oil shall be mixed to a smooth, uniform paste of uniform color throughout. The oil used may be determined by dropping from a point which has been standardized by counting the number of drops necessary to weigh 1.20 grams. The dropping shall be at a rate not greater than 70 drops per minute. The mixing shall be done by rubbing lightly with a spatula whose blade is not over 5 inches long. All the sample, blue and oil must be thoroughly incorporated. This paste shall be spread on a palette of colorless plate-glass in a layer that will not transmit light.

The standard shall be prepared in the same way and spread in a similar manner on the palette beside the sample, touching it.

Another standard paste shall be prepared by mixing 5.5 grams of the standard, 0.5 grams of ultramarine blue and 1.32 grams of bleached linseed oil in the same way and spread in a similar manner on the palette beside the sample, touching it.

In doubtful cases, only the sample and the two standards may be spread on the palette at the same time and the sample must be in contact with both standards at the edges.

To be on-grade, the sample must not be darker than the first standard and not lighter than the second standard when observed through the glass.

Settling in Water.—This test shall be made in a flat-bottomed glass tube of 11/16 inch diameter, 6 inches height and uniform bore. Twenty-seven cc. of water should fill it to a height of $4\frac{3}{4}$ inches with an allowable plus or minus variation of 1/16 inch.

Five grams of the sample shall be put into the tube after the latter is half filled with water. The product and water shall be well mixed with a piece of wire about 14 or 12 gauge and the tube filled with water to a height of $4\frac{3}{4}$ inches. The wire is to be removed and washed off in the process of adding this water. The tube shall then be shaken vigorously 80 times, the thumb being held over the opening in the top. After shaking, it shall be placed in a rack so that it stands vertically and the height of the column of the product measured at the end of 1, 2, 3 and 24 hours.

An equal amount of the standard shall be treated in the same way.

To be on-grade, the height of column of the sample must be within 10 per cent plus or minus of the height of column of the standard at the end of 24 hours.

CHAPTER XV.

ANALYSIS OF PAINT VEHICLES

Composition of Liquid Part.—The vehicle or liquid portion of paints may contain various fixed animal, vegetable or mineral oils, oleo-resinous varnishes, turpentine, mineral distillates, benzol and driers.

It is always advisable to determine the total percentage of liquids in a paint. The container should be thoroughly shaken so that the contents will be uniform throughout. A portion of 4 or 5 ounces may then be removed and placed in a screw-cap bottle. The original can of paint should then be set aside so that settling of the pigments will take place. Unless the paint is in paste form, this will usually be accomplished in twenty-four hours. A portion of the clear liquid floating over the pigments may then be removed and directly examined as outlined under Separation of Vehicle Components. See page 92. The pigment is examined in accordance with methods on page 156.

Percentage of Liquid by Ignition Method.—The percentage of vehicle in the uniform sample of paint previously obtained may be found by placing a weighed portion in a porcelain crucible and slowly igniting it to burn off the organic constituents. By carefully regulating the heat, the oil and volatile thinners will be slowly burned off, leaving the pigment behind, which may then be weighed, calculating the vehicle by difference. This method is a rapid one and works well with some pigments. When pigments are present which show an appreciable loss on ignition, or blacks or blues, this method is not to be relied upon.

Percentage of Liquid by Extraction Methods.—Another good method of separating the vehicle from a paint is to place a portion in a large tube, adding a considerable quantity of benzol, petroleum ether, or that portion of gasoline distilling below 120° C., subsequently centrifuging. Pigments which settle slowly are thrown down very rapidly by this method. The process is repeated three or four times in order thoroughly to free the pigment from oil. After drying, the pigment is weighed and the percentage of vehicle determined by difference. In case a centrifuge is not available, the vehicle of many paints may be separated by simply shaking a portion of the paint in a long test-

tube with benzol, allowing the pigment to settle, repeating the extraction until the oil is thoroughly removed.

Some operators have from time to time used Soxhlet extractor for the determination of the vehicle of a paint. This method is rather slow and does not always give satisfactory results.

It must be remembered that no method of extraction of the oil from a paint will give absolute results. The last traces of oil cannot be removed from the pigment which is probably due to the fact that many pigments such as lead and zinc react with the oil, producing small quantities of insoluble soaps which are not completely dissolved by the solvent.

In the extraction of paints, the choice of a solvent is important. When benzol (90°) is not available, it may be replaced by gasoline that has been redistilled, using the light fraction coming over below 120° C. This cannot be used, however, when varnish resins other than rosin are present, as they are insoluble therein. A good solvent often used by the writer may be made of Ethyl Ether 10 Volumes, Benzol 6 Volumes, Methyl Alcohol 4 Volumes and Acetone 1 Volume.

There are some pigments which by reason of their low specific gravity, colloidal nature or partial solubility can never be completely separated from oil, either by settling, centrifuging or extraction. Of these the most commonly met with are lampblack and other forms of carbon, zinc oxide and Prussian blue. Colloidal pigments such as zinc oxide are very troublesome in this respect. When these pigments, however, are present in a paint in considerable percentage, the difficulty of their separation may be avoided by adding to the paint three or four times its volume of fuller's earth, diluting the mixture in a large test-tube with gasoline or petroleum ether and either centrifuging or placing in a rack to settle. The fuller's earth carries down the colloidal pigments and the separation is sharp and easy This method, of course, is simply used to extract the vehicle present. The pigment resulting from the separation cannot be used for analysis on account of admixture with the fuller's earth.

In some cases the pigments in paste colors made of lampblack and Prussian blue cannot be separated from the vehicle portion. The amount of Prussian blue present, however, may may be determined by making a Kjeldahl-Gunning determination on a portion of the entire paint, multiplying the nitrogen found by 4.4. For the determination of the lampblack present,

a portion of the entire paint may be boiled with an excess of alcoholic potash until all of the oil is saponified. The mixture is then decanted through a filter and washed, first with hot alcohol and then with hot water. This affords a very good separation of the vehicle from the pigment of such paints. By this method, the Prussian blue which may be present is partially destroyed, the iron content remaining admixed with the black pigment on the filter.

Separation of Vehicle Components.—When possible, it is advisable to determine the constituents of the vehicle upon that sample that has been removed from the top of the settled can of paint. A weighed portion of this vehicle may be placed in a tared flask and attached to a Liebig condenser. Heating to 180° C. or lower will drive off nearly all the volatile constituents. The composition of the distillate may be determined by the methods given under the Examination of Turpentine. (See specifications in back of volume). A portion of the residue in the flask, which consists of oils, driers, gums, etc., may be transferred to a crucible and ignited. The residue may then be weighed and calculated to ash. The ash should be analyzed for lead, manganese and other driers.

Another portion of the original vehicle may be evaporated in an atmosphere of CO_2 (prevents oxidation) to remove the volatile constituents. A portion of the oil residue may then be examined for iodine number and other constants. In some instances it would be advisable to make a saponification and extraction of the fatty acids from this residue, determining the iodine number on the fatty acids.

Water.—For a direct determination of the percentage of water in a paint, the analyst may place a weighed quantity (approximately 100 grams) of the paint in a metal still, mixing it with an equal quantity of sand. Distillation will drive off the water and other volatile constituents which will separate into two layers in the graduate, or if no metal still is available, a direct distillation with Toluol (water saturated) may be resorted to.

Direct Distillation for Volatiles.—For a direct determination of the volatile constituents in a paint, a sample may be distilled *in vacuo.* This is easily managed wherever a vacuum pump is available and avoids the necessity of overheating the oil. When distilling by this method, a sample of the clear vehicle should not be heated above 150° C. and neither

should the solvent be volatilized in such a way as to allow the oil to be in contact with air, as it will oxidize rapidly while warm and its iodine number be very much lowered.

The following standard method for volatile, which is quick, convenient and accurate, may be used in any case and particularly where it is difficult to secure sufficient clear vehicle for distillation.

Approximately 1.5 grams varnish or 3 to 5 grams of paint are weighed by difference from a stoppered vial into a weighed shallow flat-bottom metal dish (ordinary friction top lid) 8 c.m. in diameter. The dish is heated in a well ventilated air oven at 105° to 110° C. until no further loss occurs, generally 3 hours. Loss is considered volatile thinner. In paints, any water present, as separately determined, must be allowed for.

Detection of Resinates.—To determine whether the drier in a paint is of the resinate type or linoleate type, a few drops of the oil vehicle may be mixed on a porcelain plate with one or two drops of acetic anhydride, subsequently adding a drop of sulphuric acid. Upon the addition of the sulphuric acid, a flash of purple color, turning to dark brown, will be shown where rosin is present. If rosin should be present in the vehicle to a considerable extent, the oil will have a very high acid number. The approximate percentage of rosin present may be determined by shaking a portion of the vehicle with 95 per cent alcohol in a separatory funnel, subsequently separating the alcoholic extract, evaporating and weighing the residue.

Detection of Various Oils.—Chinese wood oil may be detected in the vehicle by mixing the oil with an equal volume of a saturated solution of iodine in petroleum ether, allowing the mixture to stand in direct sunlight. Under these conditions, a peculiar, insoluble, spongy polymer of one of the fatty acids of Chinese wood oil is shown. Fish oil can usually be detected by its odor and the dark red color during saponification. The presence of soya bean and other vegetable oils is in some cases difficult to detect. The iodine numbers of these oils, however, are all lower than that of linseed oil. It must be remembered, however, that the iodine number of boiled linseed oil is lower than that of raw oil and that the iodine number of oils extracted from many paints is usually lower than shown by the original oil. In the presence of considerable quantities of drier, it is always advisable to extract the fatty acids from oil and make the iodine determination upon them. Determination of hexabromides gives best information as to type of oil present.

The distillate from the paint vehicle may consist of turpentine, mineral distillates, benzol and similar solvents. The presence of benzol is readily detected by adding a few drops of the distillate to a small quantity of a mixture of concentrated nitric and sulphuric acids. Upon heating this mixture, the characteristic ordor of nitro-benzol will be recognized if benzol is present. Mineral distillates from petroleum are easily detected by the polymerization method given under Turpentine Specifications.

CHAPTER XVI.

ANALYSIS OF PAINT OILS

Although linseed oil is used to the greatest extent in paints, some other oils occasionally find application in the manufacture of special paints. The following have been used for this purpose: soya bean oil, perilla oil, corn oil, cottonseed oil, sunflower oil, lumbang oil and similar vegetable oils; menhaden oil, whale oil, herring oil, and similar marine animal oils of relatively high iodine number.

Constants found on oils examined in the writer's laboratory are given in Table XXI.

There are given below methods for the analysis of linseed oil, in accordance with the latest practice developed by the U. S. Government Interdepartmental Committee on standardization of paint specications and the American Society for Testing Materials. These methods may be followed in examining any of the other oils mentioned above, except for iodine value on those of the *aleurites* genus.

ANALYSIS OF LINSEED AND SIMILAR OILS

Solutions Required.—The following reagents will be required:

Acetone that will pass the specification of the United States Pharmacopoeia.

Acid Calcium Chloride Solution.—Saturate with calcium chloride a mixture of 90 parts water and 10 parts HCl (sp. gr. 1.18).

Standard Sodium Thiosulfate Solution.—Dissolve pure sodium thiosulfate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 g. crystallized sodium thiosulphate will be present in 1000 cc. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, *Analytical Chemistry,* Vol. II, third edition, p. 646.) This solution will be approximately N/10 and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly N/10 strength. Preserve in a stock bottle with a guard tube filled with soda lime.

Starch Solution.—Stir up 2 or 3 g. of potato starch or 5 g. soluble starch with 100 cc. of 1 per cent salicylic acid solution, add 300 to 400 cc. boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 liter.

Potassium Iodide Solution.—Dissolve 150 g. of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

Hanus Solution.—Dissolve 13.2 g. of iodine in 1000 cc. of glacial acetic acid (99.5 per cent) that will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc. of bromine is about the proper

TABLE XXI—*Constants of Various Oils*

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Refrac. Index.
Raw Linseed Oil	.931	186	188	2.0	1.4867
Soya Bean Oil	.924	129	189	2.3	1.4813
Menhaden Oil	.932	158	187	3.9	1.4850
Raw Tung Oil	.944	166	183	3.8	1.5050
Perilla Oil	.94	200	188	2.0	1.4874
Perilla Special	.94	192	189	3.2	1.4978
Heavy Bodied Linseed Oil	.968	133	189	2.8	1.4966
Lithographic Linseed Oil	.97	102	199	2.7	1.4978
Whale Oil	.924	148	191	9.2	1.4820
Boiled Linseed Oil (Linoleate Drier)	.941	172	187	2.7	1.4895
Corn Oil	.921	124.8	190.1	4.1	1.4800
Cottonseed Oil	.920	111.7	194.3	0.9	1.4781
Rosin Oil	.964	68.9	35.5	32.4	......
Treated Tung Oil	.882	56.4	101.3	7.7	1.4764
Lumbang Oil	.927	152	189	1.0	1.4789
Sunflower Oil	.924	124.6	189.3	7.5	1.4796
Hempseed Oil	.927	149.4	191.1	3.9	1.4822
Shark Oil	.910	132.8	158.9	5.2	1.4815
Sardine Oil	.919	134.6	177.3	10.4	1.4800
Petroleum Mixing Oil	.851	28.2	52.9	1.1	1.4773
Boiled Linseed Oil (Resinate Drier)	.936	184.2	187.6	7.3	1.4895
Peanut Oil	.932	102.2	188.0	2.2	1.4790
Chia Oil	.934	196.3	192.2	0.6	1.4855
Rubberseed Oil	.924	137	193	57.0	......
Tung Oil (American)	.941	171.8	194.6	0.2	......
Japan Wood Oil	.934	154.4	193.2	0.9	1.4981
Tuna Fish Oil	.933	184	190	0.4	......
Grayfish Oil	.916	135.7	180.1	2.0	1.4703
Shark Liver Oil	.922	135.9	62.2	1.3	1.4708
Fur Seal Oil	.925	132.4	182.4	9.0	1.4772
Skate Liver Oil	.932	151.6	179.9	1.8	1.4712
Yellow Tail Fish Oil	.932	180	190	0.6	......
Salmon Fish Oil	.927	159	183	9.8	1.4788
Channel Cat Fish Oil	.923	123	192	10.9	1.4741
Palo Maria Oil	.934	96.5	193	46.1	1.4743
Soft Lumbang Oil	.938	164.2	194	4.4	1.4929
Oticia Oil	....	180.0	189	8.4	......

amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving NaOH in water in the proportion of 200 g NaOH to 200 cc. water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid (C_6H_5COOH) using phenolphthalein as indicator. (See Bureau of Standards *Scientific Paper No. 183.*) This solution will be approximately N/4, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it.

Alcoholic Sodium Hydroxide Solution.—Dissolve pure NaOH in 95 per cent ethyl alcohol in the proportion of about 22 g. per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 cc.), kept at about 50° C. for 15 days, and then distilled. For an alternate method see *Journal,* American Chemical Society, 1906, p. 395.

Half Normal Sulfuric Acid Solution.—Add about 15 cc. H_2SO_4 (sp. gr. 1.84) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized NaOH or by any other accurate method. Either adjust to exactly N/2 strength or leave as originally made, applying appropriate correction.

Methods.—The oil shall be tested in accordance with the following methods:

General.—The laboratory sample shall be thoroughly mixed by shaking, stirring, or pouring from one vessel to another and the samples for the individual tests taken from this thoroughly mixed sample.

Loss on Heating at 105 to 110° C.—Place 10 g. of the oil in an accurately weighed 200 cc. Erlenmeyer flask; weigh. Heat in an oven at a temperature between 105 and 110° C. for 30

minutes; cool and weigh. Calculate the percentage loss. This determination shall be made in a current of dry carbon dioxide gas.

Foots.—With all materials at a temperature between 20 and 27° C., mix, by shaking in a stoppered flask for exactly one minute, 25 cc. of the well-shaken sample of oil, 25 cc. of acetone and 10 cc. of the acid calcium chloride solution. Transfer the mixture to a burette where settling can take place for 24 hours. The temperature during this period should be between 20 and 27° C.

The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read in tenths of a cubic centimeter or a fraction thereof. This reading multiplied by four expresses the amount of foots present as percentage by volume of the oil taken.

Specific Gravity.—Use a pyknometer accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making the test 15.5° C., water being 1 at 15.5° C.

Acid Number.—Weigh from 5 to 10 g. of the oil. Transfer to a 300 cc. Erlenmeyer flask. Add 50 cc. of neutral 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask. Heat on a steam bath for 30 minutes. Cool and add phenophthalein indicator. Titrate to a faint permanent pink color with the standard sodium hydroxide slution. Calculate the acid number (milligrams KOH per gram of oil).

Saponification Number.—Weigh about 2 g. of the oil in a 300 cc. Erlenmeyer flask. Add 25 cc. alcoholic sodium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on the steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with N/2 H_2SO_4. Run two blanks with the alcoholic sodium hydroxide solution. These should check within 0.1 cc. N/2 H_2SO_4. From the difference between the number of cubic centimeters of N/2 H_2SO_4 required for the blank and for the determination, calculate the saponification number (milligrams KOH required for 1 g. of the oil).

Unsaponifiable Matter.—Weigh 8 to 10 g. of the oil. Transfer to a 250-cc. long-neck flask. Add 5 cc. of strong solution of sodium hydroxide (equal weights of NaOH and H_2O), and 50 cc. 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agi-

tate the flask to break up the liquid but do not project the liquid onto the sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 cc.

Transfer to a 500-cc. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc., and add 100 cc. redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500-cc. separatory funnel and repeat the process using 60 cc. of ether. After thorough separation draw off the aqueous solution into a 400-c. beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 cc. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the accumulated water rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 cc. each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250-cc. flask and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool and weigh.

Hanus Iodine Number.—Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g. (0.10 to 0.20 g.) to a 500-cc. bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc. of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc. of chloroform to each of two

Note.—The unsaponifiable oil from adulterated drying oils is volatile and will evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.

empty bottles like that used for the sample. Add to each bottle 25 cc. of the Hanus solution and let stand with occasional shaking for one-half hour. Add 10 cc. of the 15- per cent potassium iodide solution and 100 cc. of water, and titrate with standard sodium thiosulfate using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titration and the titration on the samples and the iodine value of the thiosulfate solution, calculate the iodine number of the samples tested. (Iodine number is centigrams of iodine to 1 g. of sample.)

Color.—Use Gardner-Holdt Color Meter or prepare a fresh solution of pure potassium bichromate in pure colorless H_2SO_4 (sp. gr. 1.84). This solution should be in the proportion of 1.0 g. potassium bichromate to 100 cc. (184.0 g.) H_2SO_4. Place the oil and colored solution in separate thin-walled, clear glass tubes of the same diameter (1 to 2 cm.) to a depth of not less than 2.5 cm. and compare the depths of color by looking transversely through the columns of liquid by transmitted light.

HEXABROMIDE TEST FOR DETERMINING PURITY OF LINSEED OIL

The hexabromide value of oils affords the best and possibly the only method of detecting and estimating admixtures of soya bean oil with linseed oil. This test measures the percentage of ether-insoluble brominated products yielded by the oil in question. Raw linseed oil, for instance, has a hexabromide number of approximately 46, whereas soya bean oil has a hexabromide number of usually less than 5.

The two methods (Steele and Washburn or Bailey's modification thereof) by which the hexabromide test may be made, are given below. The Bailey modification differs from the Steele and Washburn method in that an acetic acid-bromide solution is used instead of a chloroform-bromide solution. The Bailey modification also entirely eliminates the use of chloroform from the reaction mixture and does not require "amylene" or other reagent for removing the excess of bromide after the bromination of the fatty acids. The Bailey modification, however, requires the precipitated hexabromides to first stand over night in an ice chest instead of immediate washing.

STEELE AND WASHBURN METHOD

A. *Preparation of Reagents.*

The following reagents are necessary:

1. *Chloroform.*—Shake ordinary U. S. P. chloroform with several portions of water to wash out all the alcohol. Dry the product with granulated anhydrous calcium chloride over night in order to remove all traces of water. Decant from the calcium chloride and distil. Add to the distillate 3 cc. of absolute ethyl alcohol for every 100 cc. of chloroform. Keep in a stoppered brown bottle.

2. *Bromide Solution.*—Mix one part by volume of C. P. bromine* with two parts by volume of chloroform, prepared as above. This solution must be made up fresh each day because it deteriorates upon standing.

3. *Wash Ether.*—Shake ordinary ethyl ether with ten per cent of its volume of ice cold distilled water. Separate and repeat the washing three times. Dry the washed ether with fused calcium chloride overnight. Decant the ether through a folded filter into another flash and add thin slices of sodium. Warm gently on a steam bath under a reflux condenser until the evolution of gas by action of the sodium has practically ceased and bits of freshly cut sodium remain bright in the ether. Distil the ether into a dry bottle and add an excess (at least three grams per liter) of finely powdered hexabromide of the fatty acids of linseed oil previously prepared. If no hexabromide is on hand from previous determinations it may be easily prepared as follows: In a centrifuge tube dissolve about 5 grams of the fatty acids of linseed oil in 15 to 20 cc. of chloroform. Place the tube in a freezing mixture and add slowly with shaking, bromine solution until a slight red color is permanent. Add a few drops of amylene to take up excess of bromine. Whirl in a centrifuge until the precipitate has settled and then pour off the chloroform. Rub up the precipitate with 20 cc. of cold absolute ether, whirl in a centrifuge and pour off the wash ether. Repeat the washing with 3 more 20 cc. portions of ether. After drying, the hexabromide is pure enough for the preparation of wash ether. Shake at intervals for two or three hours

*The authors have observed that samples of bromine marked "C. P." often contain considerable amounts of non-volatile material. All bromine which is used must be redistilled unless it is found that 5 gms. leave no weighable residue upon evaporation.

or allow the mixture to stand over night. Then place the bottle in ice water so that the ether solution will be at zero or not about 2° C. for three hours. Decant the ether solution rapidly through a folded filter into a dry bottle and keep tightly corked in order to prevent loss of ether by evaporation.

4. *Amylene.*—This material may be purchased from the Eastman Kodak Company. It is one of the organic chemicals prepared in the laboratory of the University of Illinois. It may be prepared in small quantities from amyl alcohol by the method of Adams, Jour. Am. Chem. Soc., 1918, page 1950.

B. *Preparation of the Fatty Acids.*

Weigh approximately 50 grams of linseed oil into a 1½ liter Florence flask, and add 40 cc. NaOH solution (sp. gr. 1.4) and 40 cc. of alcohol. Place the mixture on a steam bath and heat for about ½ hour. Add 1 liter of hot distilled water and insert into the neck of the flask a 2-hole rubber stopper carrying a tube which projects into the flask so that its end is slightly above the liquid, and pass a stream of CO_2 through the tube into the flask. The soap mixture may then be heated, to remove the alcohol, either over a free flame or on the steam bath. If the free flame is used, a capillary "boiler" must be placed in the liquid, since otherwise the soap solution will bump badly. If excessive foaming takes place the current of CO_2 should be increased until it is strong enough to break up the foam. If the solution is heated on the steam bath, usually about 2 or 3 hours is required to remove the alcohol, while if it is boiled over a free flame, one-half hour is usually sufficient. After the alcohol has been removed, cool the soap solution and acidify with dilute HCl (1-1). Insert a 3-hole rubber stopper, carrying two glass tubes arranged as for a wash bottle, leaving the third hole in the stopper open for an outlet for the CO_2. The inlet tube should extend to just above the layer of fatty acids, and the outlet tube should extend to the bottom of the flask. It is essential that the outlet tube should not extend down more than an inch or two outside of the flask, as otherwise siphoning would take place, causing the liquid to boil inside the tube.

Pass a stream of CO_2 through the system, and boil gently, using a capillary boiler to prevent bumping, until the layer of fatty acids is clear. Plug the hole in the stopper which acts as an outlet for the CO_2. The lower layer will be forced out through the outlet tube by the pressure of the CO_2. In this manner remove as much water as possible without losing any of

the fatty acids, then remove the stopper and add about 500 cc. of hot distilled water, shake thoroughly so that the fatty acids are well washed, allow the fatty acids to separate and siphon off the wash water as before. Repeat the washing until the wash water does not give an acid reaction with methyl orange. Before removing the last washing, insert a capillary boiler and boil gently until the fatty acid layer is clear. After the last washing, remove the stopper and suck up with a pipette the last few globules of water. Filter the hot fatty acids through a folded filter under an evacuated bell jar and keep in a well stoppered bottle.

C. *Preparation of Hexabromides.*

Weigh accurately in a weighed centrifuge tube (approximately 6½ inches long by 1 inch in diameter) 1.00 gram (plus or minus 0.05 gram) of linseed fatty acids, prepared as given above. Dissolve in 10 cc. of chloroform and place the tube in a freezing mixture kept as near—5° C. as possible, made by adding a little dilute hydrochloric acid to finely cracked ice. Add bromine solution from a burette at the rate of one or two drops per second, shaking the tube well during the addition. At first the bromine color will be rapidly discharged, but later the mixture will assume a permanent orange color indicating a slight excess of bromine. For most fatty acids of linseed oil about 1 cc. of the bromine solution will be found necessary to give the orange color. At this point run in rapidly 0.5 cc. more of the bromine solution, shake well, and allow the tube to stand in the ice mixture for ten minutes. Remove the tube from the freezing bath and add amylene drop by drop with shaking until the bromine color has entirely disappeared. Usually five to six drops of amylene are sufficient, but a slight excess does no harm. The addition of bromine solution must never be done in direct sunlight.

Attach the tube to a good water vacuum pump (one which will indicate a pressure not greater than 40 mm. of mercury) by means of a new one-hole rubber stopper. Evaporate the chloroform in a vacuum, warming the tube in water at 50 to 60° C. to hasten evaporation. The tube must be constantly shaken to prevent bumping of the chloroform. Towards the end of the evaporation, when the contents of the tube become more viscous, rotate and tilt the tube so that the oil will flow about half way up the sides and thus present more surface for evaporation. When practically all the chloroform has been evap-

orated, place the tube in a bath at 55 to 60° C. for fifteen minutes, keeping the suction on.

Detach from the pump and place the tube in a bath of finely cracked ice and water. When the tube is cold pour down its sides 20 cc. of cold wash ether, as prepared above. The wash ether should have been previously placed in four corked test tubes graduated at 20 cc. by a file mark and kept at 0° C. in an ice bath. Thoroughly stir and rub up the bromide mixture with a rod, breaking up all the lumps. Return the tube to the ice bath for two minutes and then whirl in a centrifuge until the precipitate has settled into a hard cake and the supernatant liquid is clear. Return the tube to the ice bath for two minutes and then pour off the wash ether, making sure that no solid material is lost. Repeat the washing of the hexabromide precipitate three times in exactly the same way, using three 20 cc. portions of ice-cold wash ether and rubbing up the precipitate thoroughly each time. Use a weighed stirring rod and wash the precipitate adhering to the rod into the tube with the wash ether at each washing of the hexabromide. Afterwards dry and weigh the rod plus the slight coating of precipitate and add the weight of material on the rod to the weight of the main portion of hexabromide. After the fourth ether washing has been poured off, carefully incline and tap the tube and spread the hexabromide precipitate part way up the sides. Warm the tube in water at 50 to 60° C. until most of the ether has evaporated. Attach to the suction pump and place the tube in a bath at 60 to 70° C. for fifteen minutes. Detach the tube from the pump, cool in cold water to room temperature, wipe dry with a towel and weigh at once. Dry the tube to constant weight in an oven at 100-110° C. The total weight of the precipitate times 100 divided by the weight of fatty acids taken, gives the hexabromide percentage. The hexabromide should dry pure white.

Special Precautions:

1. Have the chloroform dry and adjust its alcohol content to three per cent.

2. Make sure that all the chloroform is evaporated from the impure hexabromide before adding wash ether. This will be accomplished if the water pump indicates a pressure not greater than 30-40 mm. and the tube is heated in the bath at 60° C. for two-thirds of its length.

3. Make sure that the wash ether is anhydrous and free from alcohol and that it is saturated with hexabromide at 0°C. Un-

less the wash ether is allowed to stand at 0° C. for a sufficient length of time before filtering off excess hexabromide, it will be super-saturated at 0° C. and will give high results. Care should be taken to prevent appreciable loss of ether by evaporation; it is well to cool the stock bottle of wash ether on hot days before uncorking.

4. Make sure that the centrifuge tube containing hexabromide and the wash ether are kept as near 0° C. as possible during the process of washing. The finely cracked ice should be replenished at intervals.

5. It has been found that low and non-concordant hexabromide results on pure linseed oil by the new method can nearly always be traced to the use of a faulty vacuum pump or to faulty rubber connections. Therefore, the operator should convince himself by test with a mercury manometer immediately before making the determination that his pump, as used, will give a vacuum of not greater than 30 mm. mercury. Heavy walled pressure tubing should always be used for connections. A faulty pump or faulty rubber connections usually means that the chloroform is not all evaporated from the impure hexabromide and will exert a solvent action on the hexabromide later on, thus giving low yields.

6. If a Nelson rotary oil pump is available, it is an excellent plan to remove the last traces of chloroform by attaching the centrifuge tube to this type of pump for 15 minutes. The bulk of the solvent should be removed first by means of the water pump.

7. With either pump the tube should be heated in a bath of 60-65°C., during the evaporation of the last traces of chloroform.

BAILEY'S MODIFICATION OF STEELE AND WASHBURN METHOD.

Hexabromide Number

References:

The literature on the determination of hexabromide numbers is not very extensive. The following are the recent references of value:

Chem. Tech. and Anal. of Oils, Fats & Waxes, by Lewkowitsch, 5th Ed., Vol. I, p. 568.

Farben Zeitung (1912) No. 3 ff.

Muggenthaler, Inaug. Dissert. 1912, Augsburg.

Bailey and Johnson, J. I. E. C. 10, 999.

Principle:

The unsaturated fatty acids when treated under proper conditions with bromine absorb at each unsaturated linkage two or more atoms of bromine depending on the degree of unsaturation. Thus at a double bond —C═C— there is obtained a saturated bromo product $-\underset{\text{Br}}{\underset{|}{\text{C}}}-\underset{\text{Br}}{\underset{|}{\text{C}}}-$ and at a triple bond —C≡C— four bromine atoms are absorbed to give a saturated compound $-\overset{\text{Br}}{\overset{|}{\underset{\text{Br}}{\underset{|}{\text{C}}}}}-\overset{\text{Br}}{\overset{|}{\underset{\text{Br}}{\underset{|}{\text{C}}}}}-$. The solubility in ether of the bromo derivaties decreases rapidly with increase of bromine content. Thus the di and tetra bromo compounds are easily soluble, whereas the hexa (and octo) compounds are only very sparingly soluble. This fact is made use of to separate the hexa (and octo) bromo derivatives in carrying out the analytical determination.

Status:

The following method is applicable to the determination of the hexabromide number of saponifiable oils. It must be remembered that the hexabromide number depends upon the method employed in making the determination. It is, therefore, important that in reporting results, the particular method must be specified.

Reagents and Apparatus:

(*a*) *Reagents:*

(1) C. P. sodium hydroxide solution of 1.4 sp. gr.
(2) 95% alcohol.
(3) Distilled water.
(4) C. P. hydrochloric acid.
(5) CO_2 or nitrogen
(6) C. P. bromine containing no non-volatile matter.
(7) Glacial acetic acid showing no reduction with dichromate or permanganate in the usual test.
(8) Wash ether.

Shake ordinary ethyl ether with 10% of its volume of ice-cold distilled water. Separate the water and repeat the washing three times. Dry the washed ether with fused calcium

chloride over night. Decant the ether through a folder filter into another flask and add thin slices of sodium. Warm gently on a steam bath under a reflux condenser until the evolution of gas by action of the sodium has practically ceased and bits of freshly cut sodium remain bright in the ether. Distill the ether into a dry bottle and add an excess (at least 3 grams per liter) of finely powdered hexabromide of the fatty acids of linseed oil previously prepared. (If no hexabromide is on hand from previous determinations, it may be prepared as follows: In a centrifuge tube dissolve about five grams of the fatty acids of linseed oil in 25 cubic centimeters of ether. Place the tube in a freezing mixture and add slowly with shaking bromine solution until a red color is permanent. Let stand for at least fifteen minutes and then whirl the tube in a centrifuge until the precipitate has settled and then pour off the ether. Rub up the precipitate with 20 cc. of cold absolute ether, whirl in a centrifuge and pour off the wash ether. Repeat the washing with 3 more 20 cubic centimeter portions of ether. After drying the hexabromide so obtained is pure enough for the preparation of the wash ether.) Shake at intervals for two or three hours or allow the mixture to stand overnight. Then place the bottle in ice water so that the ether solution will be at zero or not above 2°C. for at least three hours. Decant the ether solution rapidly through a folded filter into a dry bottle and keep tightly corked in order to prevent the loss of ether by evaporation.

(*b*) *Apparatus:*

(1) Steam bath.
(2) Gas burner.
(3) Iron tripod, ring stand and wire gauze.
(4) Round bottom flask of 2 liters capacity.
(5) Separatory funnel, 500 cc.
(6) Bell jar.
(7) Well annealed test tubes 5″ x 1″.
(8) 50 cc. burette.
(9) Glass stirring rods 6″ x 3/16″.
(10) Glass battery jars.
(11) Graduated cylinders 10 and 50 cc. capacity for weighing out samples.
(13) Centrifuge giving about 3,000 R. P. M.
(14) A vacuum showing no higher than 40 mm. pressure.

Determination:

(*a*) *Preparation of fatty acids.*—Weigh approximately 50 grams of oil into a 2 liter round-bottom flask and add 40 cc. of NaOH solution (sp. gr. 1.4=36.50% sol.) and 40 cc. of alcohol. Place the mixture on a steam bath and insert a 2-hole rubber stopper into the neck of the flask carrying a tube which projects into the flask so that its end is just above the liquid. Heat for about one-half hour, passing a stream of CO_2 through the apparatus all the while. Add one liter of hot distilled water and boil the soap solution to remove the alcohol, either over a free flame or on a steam bath. If a free flame is used about one-half hour's boiling will be sufficient, but it may be necessary to insert capillary tubes to prevent bumping of the liquid. If the solution is heated on the steam bath, usually 2 to 3 hours are required. After removing the alcohol, the solution is cooled somewhat and then acidified with dilute HCl (1:1). Warm the mixture until the fatty acids form a clear layer, continuing to pass CO_2 through the system all the time. The fatty acids are separated from the aqueous layer by means of a 500 cc. separatory funnel. The funnel is filled with the mixture, and the fatty acids will float on top, and the aqueous portion is run off. The remainder of the mixture in the flask is added to the funnel and the aqueous portion again run off. A brisk stream of CO_2 is passed into the funnel to replace the air. 300 cc. of hot distilled water is added and the mixture is vigorously shaken. After the fatty acids collect on top the aqueous portion is run off. This washing is repeated until the water is neutral to methyl orange, three washings usually being sufficient. The warm fatty acids are run into a centrifuge tube (1″ x 5″) and whirled for about one minute to collect any remaining water at the bottom. They are then filtered by decantation on to a folded filter under an evacuated bell jar and kept in a well-stoppered bottle.

(*b*) *Preparation of the hexabromides.*—Weigh accurately in a weighed centrifuge tube (1″ diam. x 5″ long) as nearly as possible one gram of fatty acids. It was found that in the case of linseed oil better results are obtained by keeping the weight of the sample as near to one gram as possible, so the deviations from this should not be more than plus or minus 0.02 gram. Dissolve the fatty acids in 25 cc. of the specially prepared ether and place the tube in a freezing mixture kept at about —5° C. made by adding a little HCl to finely cracked ice. Add bromine

solution * from a burette at the rate of about one or two drops per second, shaking the tube well during the addition until a deep red color is produced. This should not be done in direct sunlight. The tube is then allowed to stand in an ice chest overnight (about 14 hrs.), the proper precautions being taken to prevent the loss of solvent by evaporation by inserting a stopper.

It is necessary to let the tube stand for this period of time because in the case of oils which contain only a small amount of linolenic acid (soya bean oil is a good example) the precipitation of the hexabromide proceeds more slowly than in the case of an oil with a larger content of linolenic acid (linseed for example).

Next morning cool the tube by immersion in a bath of cracked ice and rub up the precipitate by means of a weighed glass rod, being sure to loosen any material adhering to the side of the tube. Whirl the tube in a centrifuge till the precipitate forms a hard cake on the bottom, cool in the ice bath, and decant the ether. Add 20 cc. of the wash ether previously prepared and cooled to 0° C. and rub up the precipitate with the glass rod. Return the tube to the ice bath and when cold whirl it in the centrifuge. Return the tube to the ice bath and then remove the ether by decantation. Repeat this washing twice more. After the last washing incline the tube and carefully tap it to spread the hexabromide precipitate part of the way up the sides. Warm the tube in water at 60°C. until most of the ether has evaporated, then attach it for 15 minutes to a vacuum line showing a pressure of 30-40 mm. keeping the temperature around 60°C. Wipe the tube dry and allow it to stand in the balance at least 15 minutes before weighing. To the weight of the precipitate in the tube add the weight of the slight amount adhering to the glass rod. This total weight of precipitate multiplied by 100 and divided by the weight of fatty acids taken, gives the hexabromide percentage.

Notes: (1) The fatty acids are used instead of the glyceryl esters because the latter give inconcordant results.

(2) In the case of linseed oil, the weight of the sample should be kept as near one gram as possible.

(3) Care should be exercised in preparing the wash ether for if it is unsaturated with hexabromides according to directions, the results will be low.

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*5 cc. bromine, 25 cc. glacial acetic acid made up just before use.

CO-OPERATIVE WORK ON HEXABROMIDE METHODS AS CONDUCTED BY SUB-COMMITTEE III OF COMMITTEE D-1, A. S. T. M.

TABLE XXII—*The results of various observers working on the two methods are given in the table below—hexabromide values*

Oils.	Steele-Washburn Method									Bailey Modification of Steele-Washburn Method.		
	Gardner and Bielouss.	Steele.	Came.	White and Crowley	Bailey.	P. and J. Waldstein.	Maximum.	Minimum.	Average.	Came.	Bailey.	Average.
100 per cent Pure Raw Linseed Oil....	45.9	46.4	46.6	45.4	46.0	46.2	46.6	45.4	46.1	40.5	42.7	41.6
85 per cent Pure Raw Linseed Oil... 15 per cent Soya Bean Oil.........	39.3	....	41.8	39.1	41.9	39.8	41.9	39.1	40.4	34.9	37.5	36.2
75 per cent Pure Raw Linseed Oil... 25 per cent Soya Bean Oil.........	36.4	38.4	38.2	36.0	37.2	36.1	38.4	36.0	37.0	31.5	34.5	33.0
65 per cent Pure Raw Linseed Oil... 35 per cent Soya Bean Oil.........	30.8	33.4	34.8	30.5	33.8	33.5	34.8	30.5	32.8	26.7	31.4	29.6

Comments made by the various observers are abstracted herewith:

"S. and P. Waldstein state that when a large percentage of soya bean oil is present in an oil there is formed a large percentage of tetrabromide which may not be completely washed out. They recommend in such instances to increase the portions of ether to 25 or 30 cc. or to increase the number of washings to 5 or 6 in order to overcome high results.

"The chairman of the sub-committee has done some experimental work with the idea of developing a method of determining the hexabromide value of oils volumetrically. It was found that the bromine absorption number of the fatty acids of linseed oil were higher than for soya bean oil in some preliminary volumetric work. It is known that the bromine substitution number of linseed oil fatty acids is low while the fatty acids of soya bean oil have a low addition number. Considerable further work, however, will be necessary in order to develop a method that will be satisfactory."

Conclusions.—The Steele-Washburn method of determining hexabromides has given closely concordant results in the hands

TABLE XXIII—*Iodine and hexabromide numbers of raw and treated linseed oils*

OL No.	Substance	Iodine No. Hanus	Hexabromide No. Steele Method		Hexabromide No. Bailey Method
			By A.	By B.	By B.
553	Linseed oil from North American seed....	176.2	42.0	43.3	42.6
553	“ “ “ “ “ “	....	45.6	41.3	41.9
553	“ “ “ “ “ “	....	46.3	45.1	
553	“ “ “ “ “ “	....	46.5	43.8	
553	“ “ “ “ “ “	....	46.3	45.5	
553	“ “ “ “ “ “	....	43.6	44.4	
553	“ “ “ “ “ “	....	39.2		
553	“ “ “ “ “ “	....	39.1		
565	Linseed oil, commercial refined..........	176.5	44.0		
563	“ “ “ raw..............	185.0	43.6	40.0	
563	“ “ “ “	....	43.8		
563	“ “ “ “	....	40.5		
574	Linseed oil (Bu. of Stds. sample).........	183.0	47.6	47.5	
574	“ “ “ “ “ “	....	49.6	45.2	
574	“ “ “ “ “ “	....	47.1	47.3	
574	“ “ “ “ “ “	....	46.9		
574	“ “ “ “ “ “	....	46.2		
574	“ “ “ “ “ “	....	45.7		
535	Lins'd oil Ext'd from Argentine seed......	189.8	50.0	49.7	
535	“ “ “ “ “ “	....	......	50.8	
535	“ “ “ “ “ “	....	......	50.7	
641	OL 553 + 5% (1) tung oil drier.........	166.8	......	45.2	42.6
641	“ “ “ “ “ “	....	......	45.9	41.1
642	“ “ + 10% “ “ “	161.5	......	44.4	41.0
642	“ “ “ “ “ “	....	......	44.1	40.9
643	“ “ + 20% “ “ “	152.5	......	41.8	39.2
643	“ “ “ “ “ “	....	......	42.2	39.0
644	“ “ + 5% grinding japan...........	164.8	......	39.7	40.8
644	“ “ “ “ “	....	......	39.6	39.2
645	“ “ + 10% “ “	158.9	......	42.3	39.9
645	“ “ “ “ “	....	......	41.1	40.3
646	“ “ + 20% “ “	147.4	......	40.4	39.9
646	“ “ “ “ “	....	......	39.4	39.4
588	“ “ + 10% (1) linoleate drier........	165.6	43.6		
588	“ “ “ “ “	....	42.7		
589	“ “ + 20% (1) “ “	169.3	45.3		
589	“ “ “ “ “	....	42.7		
589	“ “ “ “ “	....	43.6		
583	“ “ + 0.2% manganese drier*........	168.6	32.4		
583	“ “ “ “ “	....	34.7		
584	“ “ + 0.05% “ “	171.0	32.6		
584	“ “ “ “ “	....	33.2		
561	Linseed oil, commercial.................	173.8	41.8	......	42.6
561	“ “ boiled......................	....	......	......	41.9
359	“ “ heavy bodied................	80.8	11.8		

(1) Added without treating oil.
(*) Manganese linoleate boiled in at 250° C.

of several different operators, and is apparently well adapted for determining the purity of raw linseed oil. It is recommended that further work be carried on with the object of shortening the method.

Henry A. Gardner,
Chairman.

Through the kindness of Mr. Herbert S. Bailey and Mr. Baldsiefen of the Experimental Station, E. I. du Pont de Nemours &Co., there are presented herewith two tables (XXIII and XXIV) showing the iodine and hexabromide numbers of raw and treated linseed oils, and of soya bean oil, tung oil, and various mixtures thereof. It is believed that the data presented in these tables will be of great service to the paint chemist who intends to carry on hexabromide work.

Table XXIV—*Iodine and hexabromide numbers of soya bean, tung and linseed-soya bean mixtures*

OL No.	Substance	Iodine No. Hanus	Hexabromide No. Steele Method		Hexabromide No. Bailey Method
			By A.	By B.	By B.
310	Soya bean oil, raw	133.2	5.1	6.5	4.2
310	“ “ “ “		6.1		4.9
310	“ “ “ “		6.3		3.6
565	Soya bean oil, raw commercial	133.2	1.5		
565	“ “ “ “ “		5.0		
658	Soya bean oil, cold pressed			8.41	7.27
658	“ “ “ “ “			9.38	7.54
659	Soya bean oil, cold pressed			5.95	5.35
659	“ “ “ “ “			5.76	5.65
670	Soya bean oil, extracted			3.9	
622	Tung oil			0.0	0.0
572	50% OL 553 + 50% OL 310		26.0	23.0	
572	“ “ “ “ “ “			23.6	
572	50% OL 553 + 50% OL 670			24.3	23.3
572	“ “ “ “ “ “			24.6	24.3

CHAPTER XVII.

EXAMINATION OF FLAXSEED*

Sample is quartered until 500 grams are obtained. In quartering, seed must be poured at center of pile to evenly distribute seed and impurities. All of the dirt which settles to the bottom must be carefully brushed up and added to the pile. Screen the 500 gram sample through 10 mesh until about 50 grams is hand picked and everything other than linseed is set aside and weighed with the dust. The clean seed obtained at this picking is added to what has passed through the 10 mesh screen. The seed is then passed through a 20-mesh screen, rubbing the seed around in the screen so as to remove any seed attached to it. The under size is collected and weighed after the coarse pickings have been added to it. This constitutes the first dust. Partially clean linseed is then reduced to 50 grams in a riffle sampler. This is divided into two 25-gram portions which are hand picked separately and the impurities weighed separately. All seed, whether dried seed or broken seed, is to be put with the linseed. After corrected calculation, the total impurities are obtained. The impurities found in the second picking should agree within 60 milligrams.

Oil in Flaxseed.—A 3-gram sample of the clean seed is weighed out and is ground in an agate mortar with an equal part of fine sea-sand which has been washed with hydrochloric acid. The ground sample is placed in a Soxlet thimble and extracted with redistilled ether for three hours. The distillate is placed in a weighing dish and the ether is removed by evaporation. The residue is then dried for one-half hour at 103° C., and the oil is weighed.

Oil in Oil Cake.—A 10-gram sample of undried oil cake is placed in a Soxlet thimble and extracted in the same way as described under Oil in Flaxseed.

Water in Oil Cake.—Weigh 5 grams of oil cake and place in flask fitted with clean cork. Weigh flask, cork and contents; connect with hydrogen generator, and start flow of hydrogen at the rate of 2 bubbles per second. Place flask in paraffin bath at a temperature of 110° C., and heat in current of hydrogen

* Contributed by R. L. Hallett.

for two hours. Disconnect tubing, and wipe clean of paraffin while hot, with absorbent paper. Cool and draw dry air through flask to remove hydrogen. Disconnect, replace original cork, and weigh. Loss of weight reported as moisture.

Protein in Oil Cake.—Protein is found by determining total nitrogen by Kjeldahl, calculating it to protein.

CHAPTER XVIII.

SPECIFICATIONS FOR RAW TUNG OIL AND METHODS OF TEST

PROPERTIES AND TESTS, A. S. T. M. 1922

Raw tung oil shall conform to the following requirements:

	Maximum.	*Minimum.*
Specific gravity at $\frac{15.5^\circ}{15.5^\circ}$ C	0.943	0.939
Acid number (Alcohol-Benzol)	7	.....
Saponification number	195	190
Unsaponifiable matter, per cent	0.75	.....
Refractive index at 25° C	1.520	1.515
Iodine number (Wijs)	.....	163
Heating test, minutes	12	.....

METHODS OF TESTING

Solutions Required.—The following reagents will be required:

Standard Sodium Thiosulfate Solution.—Dissolve pure sodium thiosulfate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 g. crystallized sodium thiosulfate will be present in 1000 cc. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, *Analytical Chemistry,* Vol. II, third edition, p. 646.) This solution will be approximately N/10 and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly N/10 strength. Preserve in a stock bottle with a guard tube filled with soda lime.

Starch Solution.—Stir up 2 to 3 g. of potato starch or 5 g. soluble starch with 100 cc. of 1-per-cent salicylic acid solution, add 300 to 400 cc. boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 liter.

Potassium Iodide Solution.—Dissolve 150 g. of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

Iodine-Monochloride Solution.—Dissolve iodine in glacial acetic acid that has a melting point of 14.7 to 15°C. and is free from reducing impurities in the proportion so that 13 g. of iodine will be present in 1000 cc. of the solution. The prepara-

tion of the iodine-monochloride solution presents no great difficulty, but it shall be done with care and accuracy in order to obtain satisfactory results. There shall be in the solution no sensible excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary. Set aside a small portion of this solution, while pure, and pass dry chlorine into the remainder until the halogen content of the whole solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged, there will be a slight excess of chlorine, which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

Chloroform.—Should be U. S. P.

Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving NaOH in water in the proportion of 200 g. NaOH to 200 cc. water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175cc. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid (C_6H_5COOH) using phenolphthalein as indicator. (See Bureau of Standards *Scientific Paper No. 183.*) This solution will be approximately N/4, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it.

Alcoholic Sodium Hydroxide Solution.—Dissolve pure NaOH in 95-per-cent ethyl alcohol in the proportion of about 22 g. per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 cc.), kept at about 50°C. for

15 days, and then distilled. For an alternate method see *Journal,* American Chemical Society, 1906, p. 395.

Half Normal Sulfuric Acid Solution.—Add about 15 cc. H_2SO_4 (sp. gr. 1.84) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized NaOH or by any other accurate method. Either adjust to exactly N/2 strength or leave as originally made, applying appropriate correction.

Methods.—The oil shall be tested in accordance with the following methods:

General.—The laboratory sample shall be thoroughly mixed by shaking, stirring, or pouring from one vessel to another and the samples for the individual tests taken from this thoroughly mixed sample.

Specific Gravity.—Use a pyknometer accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making the test at 15.5° C., water being 1 at 15.5°C.

Acid Number.—Weigh from 5 to 10 g. of the oil. Transfer to a 300-cc. Erlenmeyer flask. Add 50 cc. of a mixture of equal parts by volume of 95-per-cent ethyl alcohol and c. p. reagent benzol. (*This mixture should be previously titrated to a very faint pink with dilute alkali solution, using phenolphthalein as an indicator*). Add phenolphthalein indicator and titrate at once to a faint permanent pink color with the standard sodium hydroxide solution. Calculate the acid number (milligrams KOH per gram of oil).

Saponification Number.—Weigh about 2 g. of the oil in a 300-cc. Erlenmeyer flask. Add 25 cc. alcoholic sodium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on the steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with N/2 H_2SO_4. Run two blanks with the alcoholic sodium hydroxide solution. These should check within 0.1 cc. N/2 H_2SO_4. From the difference between the number of cubic centimeters of N/2 H_2SO_4 required for the blank and for the determination, calculate the saponification number (milligrams KOH required for 1 g. of the oil).

Unsaponifiable Matter.—Weigh 8 to 10 g. of the oil. Transfer to a 250-cc. long-neck flask. Add 5 cc. of strong solution of sodium hydroxide (equal weights of NaOH and H_2O), and 50 cc. 95-per-cent ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agitate the flask to break up the liquid but do not project the liquid onto the

sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 cc.

Transfer to a 500-cc. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc., add 100 cc. redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500-cc. separatory funnel and repeat the process, using 60 cc. of ether. After thorough separation draw off the aqueous solution into a 400-cc. beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 cc. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the accumulated water rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 cc. each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250-cc. flask and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool and weigh.

Refractive Index.—Use a properly standardized Abbé refractometer at 25° C., or any other equally accurate instrument.

Iodine Number.—Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping from 0.16 to 0.19 g. to a 500-cc. bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine tests. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc. of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc. of chloroform to each of two empty bottles like that used

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Note.—The unsaponifiable oil from adulterated drying oils is volatile and will evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.

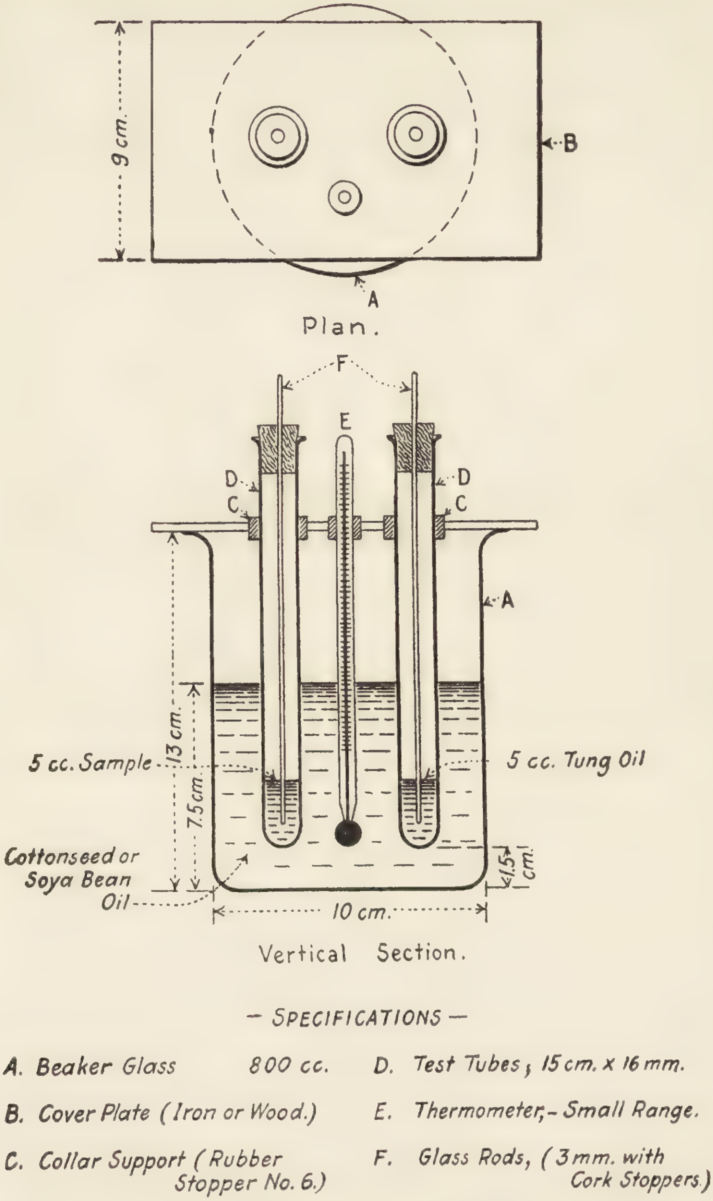

FIG. 47—Tung Oil Heat Test Apparatus (Revised 1920)

Note.—Collars *C* may be omitted and tubes supported in present place by aid of wire gauze placed in bottom of oil bath and resting on bottom of beaker.

for the sample. Add to each bottle 25 cc. of the Wijs solution and let stand with occasional shaking for 30 minutes in a dark place at a temperature of from 21 to 23° C. Add 10 cc. of the 15-per-cent potassium iodide solution and 100 cc. of water, and titrate with standard sodium thiosulfate using starch as the indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titration and the titration on the samples and the iodine value of the thiosulfate solution, calculate the iodine number of the samples tested. (Iodine number is given in centigrams of iodine to 1 g. of sample.) *

Heating Test.—Test tubes containing the oil should be 15 cm. by 16 mm., with a mark near the bottom to indicate 5 cc., and closed by a cork so perforated that a glass rod 3 mm. in diameter can move freely.

Fill an 800-cc. glass beaker (height, 13 cm.; diameter, 10 cm.) with cottonseed oil or soya bean oil to a height of 7.5 cm. Place a thermometer so as to be 1.5 cm. from the bottom of the bath.

Use a nitrogen-filled, chemical thermometer; engraved stem; total length 4 to 4½ in., graduated from 210 to 310° C. in 2° intervals; the length between 210 and 310° C. not less than 2½ in. Thermometer glass shall be well annealed.

When the bath temperature is 293° C. (560° F.) and very slowly rising at this point, place the tube containing 5 cc. of the oil to be tested and the tube containing 5 cc. of a control sample of known value, so that the bottom of each tube is level with the lowest part of the bulb of the thermometer. If desired, the collars *C* may be omitted and the tubes allowed to rest upon a piece of wire gauze placed in the bottom of the oil bath so that the tubes will be 1.5 cm. from the bottom of the bath. Note the time. Remove the source of heat for about 45 seconds and then reapply. Before 2 minutes have elapsed the temperature of the bath will have fallen to 282° C. (530° F.), at which point it should be kept as steady as possible. When the samples have been in the bath 9 minutes, raise the glass rods at intervals of ¼ minute. Note the time when each sample becomes firmly set. At this period the oil will be so stiff that the entire tube may be lifted by aid of the rod if the collar *C* is omitted from the apparatus. As setting or jellying takes place within a few seconds of fluidity, a good end determination is afforded. Remove the

* It is always well to include a test on a sample of tung oil of known iodine value. This may be kept in a dark-colored bottle as a standard.

specimens. Heat the bath again to 293° C., and repeat the experiment with fresh portions of the sample.

No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached. When the bath oil has become tarry and viscid, it should be renewed; otherwise heating may be irregular.

Open-Pan Heat Tests.—Open-pan heat tests for quality of tung oil, as used by well known chemists, are also described below. These tests offer additional information regarding the character of the oil and its suitability for use in varnish making.

> *Bacon Test.*—One hundred grams of oil are weighed into a saucepan about 5 in. in diameter and about 2¼ in. deep. The weighed oil is placed over a flame and stirred, and when it reaches 280° C. the time is noted. It is maintained at this temperature with stirring, using the thermometer, and the time of solidification noted, as well as the resultant product and its general behavior, color and cutting qualities. Pure oil is always run as a control and for comparison. Pure oil will invariably solidify in from 4¾ to 7¾ minutes; doped oil will usually require 7 minutes or more, and will behave in a manner differing from that of pure oil.
>
> *Worstall Test.*—Place about 100 grams of china wood oil in an open metal pan of such diameter that the oil will be at least one inch in depth. It is more important to have the layer of oil an inch deep than it is to have an exact weight of it. The oil in this pan is heated as rapidly as possible to a temperature of 540° F. With the usual gas burners available in the laboratory, this rise in temperature can be accomplished in about four minutes. The time is noted when the thermometer shows the oil in the pan to be at 540°. The oil is stirred with the thermometer until it starts to string or solidify. This time should, as a rule, not exceed 7½ minutes, though occasionally oils which work satisfactorily may require as much as 8 or 8¼ minutes. As soon as the oil has developed a decided string, it is stirred with a stiff spatula until solid. It is held for one minute at this temperature. The solidified oil is then removed from the pan and a cubic inch from the center is removed. This should be pale in color and firm. When cut with a spatula the surface should be dry and not sticky and the appearance of it should be dull rather than bright. The mass, when rubbed, should powder like dry bread. Adulterated oil will frequently take an excessive time to solidify and will yield a gel which is soft, is sticky when cut, and the cut surface of which is bright and shiny. The color of the gelled mass is frequently darker than if the oil is pure.

CHAPTER XIX.

ANALYSIS OF VARNISH

The testing of varnish should largely be of a physical nature. Such properties as odor, consistency, clarity, flowing, time of drying, character of finish, hardness, resistance to moisture and abrasion, elasticity, etc., point out the real value of a varnish. Chemical tests that give additional information, sometimes of a valuable nature, are as follows: Flash point, acid number, ash, character of solvent, fixed oil and resins.

Flash Point.—A nickel or iron crucible of 60 mm. diameter and 40 mm. height is filled with the varnish to within 20 mm. of the top. It is then supported in a water bath in such a manner as to be about two-thirds immersed in the water. The water should be from 15° to 20° C. at the start and should be heated slowly so that the temperature of the varnish, as indicated by a thermometer suspended in it, will show a rise of about 1 degree per minute. Test for flash at each half degree, using a very small flame. (See also A. S. T. M. use of Tag closed tester.)

Acid Number.—Ten to 20 grams of the varnish are weighed into a small Erlenmeyer flask, 50 cc. neutral alcohol added, and a small funnel inserted in the neck. Heat on the water bath for one-half hour, with occasional shaking. Allow to cool somewhat, add two drops of phenolphthalein indicator and titrate with tenth-normal potassium hydroxide solution. The acid number is the number of milligrams of KOH required to neutralize each gram of the varnish. Use of a mixture of equal volumes of alcohol and benzol 90° gives the true acid number of a varnish including colloidal acidity that would not be indicated by alcohol alone.

Ash.—Weigh in a porcelain or fused silica crucible several grams of the varnish. Burn off over a small Bunsen flame, using great caution to avoid boiling over and spattering. When all combustible matter is destroyed, weigh the ash and if desired analyze it.

Solvent.—Steam distillation of a portion of the varnish will remove the solvents, leaving a residue of fixed oils and varnish resins, which may be weighed after driving off the water. The distillate should be examined as recommended under Turpentine Specifications. The amount of mineral spirits and turpentine may thus be determined.

It is customary to conduct the steam distillation upon 50 grams of varnish in a 500-cc. Erlenmeyer flask placed in an oil bath maintained at about 130° F. The distillate may be collected in a separatory funnel. The water may then be drawn off and the distillate examined.

A much more rapid and fully as accurate a method for determining the percentage of volatile is as follows. This method, however, does not yield the actual volatile for subsequent examination.

Percentage of Volatile.—Place a portion of the sample in a stoppered bottle. Weigh the container and sample. Transfer about 1.5 grams of the sample to a flat bottom metal dish about 8 cm. in diameter (a friction top can plug). Weigh the bottle again and by difference calculate the exact weight of the portion of the sample transferred to the metal dish. Heat the dish and contents in an oven maintained at 105° to 110° C. for 3 hours. Cool and weigh. From the weight of the residue left in the dish and the weight of the sample taken, calculate the percentage of non-volatile residue.

Fixed Oils and Resins.—In the above determination, the total amount of fixed oils and resins is obtained. It is a difficult matter, however, to determine the exact percentage and character of resins that have been used in the manufacture of the varnish. This is due to the fact that during the process of heating oils in the presence of resins many intricate chemical changes are brought about, a considerable portion of the resins being distilled off in the form of vapors and combinations of the oil brought about that are difficult of separation. One of the best methods, however, of separating the fixed oils and varnish resins is carried out in the following manner:

A portion of about a half ounce of the varnish resin should be placed in a 300-cc. tared beaker. There should then be added about 200 cc. of ice-cold petroleum ether. After stirring the beaker should be covered and allowed to stand, preferably in a dish containing ice. In an hour's time the resinous ingredients will be found precipitated at the bottom of the beaker or adhering to the side thereof (with the exception of rosin, which is largely soluble in petroleum ether). The precipitated resins should be washed with fresh portions of cold petroleum ether two or three times, pouring the decanted portions into a large bottle. The combined portions of petroleum ether may then be filtered through a tared filter, adding by the aid of a stirring rod the resins contained in

the beaker. The filter paper and the beaker with the resins may they be dried at 100° C. and weighed. The combined filtrates may be distilled to obtain the fixed oil as a residue, which may be examined for constants. (This fixed oil may contain rosin.) The amount of rosin contained in a varnish may be roughly ascertained by thoroughly shaking in a separatory funnel a portion of the varnish with a large quantity of absolute alcohol. The rosin may be obtained by evaporation of the alcoholic extracts. The fixed oils after oxidation or polymerization, as caused by the heating of the varnish during manufacture, are not readily soluble in alcohol.

Separation of Polymerized Oils and Resins.—In the making of varnish, most oils become oxidized or polymerized to a condition resembling resins. For instance, when a varnish is examined for resins by the above method, it will often be found that a considerable amount of matter insoluble in petroleum ether will be obtained even when hard resins are absent. The insoluble substance is oxidized or polymerized oil. It may be differentiated from varnish resins by the fact that it may be saponified by alcoholic potash.

This method, as used by the regulatory division of the State of North Dakota, is the original method published by E. W. Boughton of the Bureau of Standards (see U. S. Bureau of Standards Technologic Bulletin 65), as modified in North Dakota. Although it involves a tremendous amount of work, it is probably the most accurate method for the separation of polymerized oils and resins. The method follows Boughton's original scheme very closely. The use, however, of ice-cold ether and ice-cold water is probably an advantage in that the ether separations are quicker and sharper. In Boughton's original method, the material extracted by ether from the first saponification mixture of acids and fatty acid soaps is termed unsaponifiable matter. In the North Dakota revision, the proposal is made to add this same ether extract to the resin portion. This constitutes a somewhat radical difference between the two schemes and clearly brings out the fact that neither Boughton's method nor the North Dakota method can be relied upon to give the true oil content of present-day varnishes. For instance, at least one of the varnishes on the market today contains wool fat (degras). In Boughton's method this product would show up as unsaponifiable matter, while in the North Dakota method the unsaponifiable part of the wool fat would be included in the resins. This same difference would be true of a varnish con-

taining paraffin. On the other hand, a varnish made of tung oil and cumarin resin would show a high unsaponifiable and resin content by Boughton's method, while the North Dakota method would indicate the cumarin as resin.

In view of the above, it is quite apparent that neither one of these methods should be included as a part of any routine method of analysis of a varnish but should be merely classed as "stunt" tests for a research laboratory, where an insight into the ingredients of a varnish is desired. All of which brings out the absolute futility of varnish analysis as a basis of evaluation. Physical tests afford the only reliable data in judging the properties of an oleo-resinous varnish.

Method.—Weigh by difference from 4 to 6 grams of the varnish into a 125-cc. Erlenmeyer flask, add 25 cc. of water and boil gently until not over 5 cc. of water is left. This is best performed by placing the flask in an oil bath, and by passing a stream of carbon dioxide through the mixture during the evaporation. Then add 25 cc. each of half normal alcoholic potash and benzol, and reflux for one hour.

Evaporate the solution down to about 10 cc. and transfer to a 500-cc. globe-shaped separatory funnel, rinsing the flask well with water, alcohol and ether. Add 100 cc. each of water and ethyl ether and shake well, using a moderate circular motion. In this and all similar operations use ice-cold ether and ice-cold water. The shaking should be repeated three times. Should an emulsion form and not break within five minutes, add 2 cc. of alcohol.

Draw off the aqueous layer into another separatory funnel and wash the ether layer twice with cold water. Add the washings to the aqueous layer and transfer the ether layer to a weighed Erlenmeyer flask labeled "Gums." Acidify the aqueous layer and completely extract with ether. Transfer the ether solution to the Erlenmeyer flask into which the varnish was weighed and distill off the solvent, using a vertical condenser. Then add 10 cc. absolute alcohol and evaporate on a steam bath. This is to remove the water present. Distill off the solvent in the "Gums" flask whenever the flask becomes half-full. All ether solutions of unsaponifiable matters and the resins acids that are separated out from subsequent extractions are transferred to this flask.

To the residue extracted from the acid solution add 20 cc. of absolute alcohol and 20 cc. of a mixture of 4 parts of absolute alcohol and 1 part of concentrated sulphuric acid. Reflux for

five minutes, transfer to a separatory funnel, rinsing the flask with water and ether, and add 100 cc. of ether. Shake well, add 100 cc. of a 10-per-cent solution of sodium chloride, and shake several times. Draw off the aqueous layer and extract with 50 cc. of ether. Wash the combined ether layer and discard the aqueous layers. To the ether layer add 50 cc. fifth normal aqueous potassium hydroxide and 10 cc. of alcohol and shake well, using a moderate circular motion. Repeat the shaking as soon as the layers have separated. Separate the layers and wash the ether layer with 50 cc. of water containing 5 cc. of the aqueous potassium hydroxide and 5 cc. of alcohol.

Combine the aqueous layers and extract with ether keeping all insoluble soaps with the ether layer. Then combine the ether layers, transfer to an Erlenmeyer flask, and distill off the solvent. Take the aqueous layers, acidify with hydrochloric acid and extract completely with ether. Transfer this ether solutions to the "Gums" flask.

Take the residue and reflux with 25 cc. of alcoholic potash for one hour. Evaporate on steam bath until only 10 cc. remains. Cool, transfer to a separatory funnel with the aid of 50 cc. each water and ether and shake. Use the same moderate circular motion. Repeat the shaking twice and draw off the aqueous layer. Extract the aqueous layer with ether again. Combine the ether layers and wash twice with 600 cc. portions of water. Transfer the ether layers to the "Gums" flask. Take the aqueous layer and the washings from the ether layer, acidify with hydrochloric acid and extract completely with ether. Transfer these ether extracts to a weighed Erlenmeyer flask, distill off the solvent and heat on a steam bath with small portions of absolute alcohol until all of the water is removed. Then heat to constant weight at 105° C., in an oven filled with carbon dioxide. Weigh as *fatty acids.*

Take the "Gums" flask, distill off the solvent, remove the water, dry and weigh as in the case of the fatty acids. This weight is reported as resins or as varnish gums.

Calculations:

(a) $\dfrac{\text{Wt. of Resins} \times 1.07}{\text{Wt. of sample}} \times 100 =$ percent total of resins (direct).

(b) $\dfrac{\text{Wt. of fatty acids}}{\text{Wt. of sample}} \times 100 =$ percent of total oils.

(c) (Percent of non-volatile − percent of ash) = percent of total resins (by difference).

CHAPTER XX.

ANALYSIS OF MIXED DRIERS

While composed mainly of organic material, mixed driers may contain silicon, iron, aluminum, calcium, magnesium, phosphorus, copper, zinc, lead, manganese and cobalt. Some of these are present in linseed oil, oils and resins, some may be accidentally introduced (as from kettles) and some are purposely added. Although the last three only are usually determined, the possible interference of the others must be considered in any scheme of analysis.

When an accurate determination of the percentage of various metallic driers in oils and varnishes is desired, it is customary to ignite the mass and examine the ash. Wet oxidation, of such large amounts of sample as are necessary, with nitric and sulphuric acids is impracticable and rapid ignition at high temperatures will result in the volatilization of some or all of elements such as lead and zinc.

The ash is usually extracted with nitric acid, on account of the presence of lead. It is to be borne in mind that direct determination of lead as sulphate is not permissible in the presence of calcium, that the bismuthate method for manganese can not be used in the presence of cobalt, and that most methods for the determination of cobalt require the elimination of several of the above constituents.

RECOMMENDED PROCEDURE*

(For lead, manganese and cobalt)

Ash 50-200 g. of the drier in a muffle at the lowest possible temperature. Dissolve the ash in dilute nitric acid (1:1), adding hydrogen peroxide to facilitate solution in case peroxides are present. Filter and dilute to measured volume.

Determine manganese in an aliquot of the above solution by the persulphate-arsenite method if cobalt is present and by either this method or the bismuthate method in the absence of cobalt. (A. S. T. M. Standards, 1921, pages 514-16).

Determine lead in another aliquot by first precipitating with hydrogen sulphide in a solution of suitable acidity, dissolving the precipitate in hydrochloric acid with the aid of a little

* Suggested by P. H. Walker.

nitric acid toward the end, if necessary, and then finally precipitating the lead as sulphate or as chromate by the usual procedures.

Determine cobalt in another aliquot by first evaporating with sulphuric acid to eliminate lead, then carrying on a double precipitate with ammonia to eliminate iron and aluminum, and finally adding potassium nitrite to the combined ammoniacal filtrates after acidification with acetic acid. In case the amount of cobalt is very small, a preliminary concentration should be carried out by treating the ammoniacal filtrates with ammonium sulphide, filtering, dissolving the sulphides, making the solution alkaline and then proceeding with the acidification and addition of nitrite.

If a determination of zinc is desired, it may be carried out in the filtrate from the hydrogen sulphide separation of lead. In this case, the filtrate should be treated with sulphuric acid and evaporated until sulphuric acid is evolved. The cooled solution should then be diluted, neutralized until it contains approximately one hundredth normal sulphuric acid and zinc precipitated in the sulphide which can then be ignited and weighed as oxide or sulphate. For determining the efficiency of a drier, see methods outlined under Interdepartmental Specifications for Drier, back of this volume.

Quick Test for Driers in Varnishes and Pigmented Enamels.— A quick test communicated to the writer by C. L. Schumann,* for determining such constituents, is as follows:

Weigh 50 grams of varnish into a 500 cc. Erlenmeyer flask, add 60 cc. of denatured alcohol, 60 cc. concentrated hydrochloric acid, and a few glass beads. Heat on a hot plate until most of the alcohol is boiled off. Add about 12 oz. of water and heat to boiling, subsequently filling up to the neck of the flask with turpentine substitute. Heat and let stand until a clear separation is noted. Siphon off the turpentine substitute and add another portion thereof. Repeat process. Evaporate the water solution to a sufficient concentration for determining metals present. This water solution will contain all the metal portion of the varnish. The same method as above may be used with enamels, but only 2 to 3 grams is required.

* Pratt and Lambert Laboratories.

CHAPTER XXI.

CHEMICAL EXAMINATION OF SHELLAC*

DETERMINATION OF ROSIN

Solutions Required.—The solutions required are one of iodine monochloride contain 13 g. of iodine per liter, in glacial acetic acid that has a melting point of 14.7 to 15° C. and is free from reducing impurities; and another of sodium thiosulfate, made by dissolving 24.83 g. of the pure salt in a liter of water. In addition to these solutions there is required a quantity of acetic acid of the same strength as that used for making the solution of iodine monochloride. Pure chloroform and starch are also necessary.

The preparation of the iodine-monochloride solution presents no great difficulty, but it shall be done with care and accuracy in order to obtain satisfactory results. There shall be in the solution no sensible excess either of iodine or more particularly of chlorine, over that required to form the monochloride. This condition is most satisfactorily attained by dissolving in the whole of the acetic acid to be used the requisite quantity of iodine, using a gentle heat to assist the solution, if it is found necessary. Set aside a small portion of this solution, while pure, and pass dry chlorine into the remainder until the halogen content of the whole solution is doubled. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the characteristic color of free iodine has just been discharged, there will be a slight excess of chlorine, which is corrected by the addition of the requisite amount of the unchlorinated portion until all free chlorine has been destroyed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

Method.—Introduce 0.2 g. of ground shellac into a 250-cc. dry bottle of clear glass with a ground-glass stopper, add 20 cc. of glacial acetic acid (melting point 14.7 to 15° C.) and warm the mixture gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble; solution is quicker according to the proportion of rosin present. Add 10 cc. of chloroform and cool the solution to 21 to 24° C. The

* A. S. T. M. Method with Changes as recommended by Chemists' Committee of the United States Shellac Importers' Association.

temperature should be held well within these limits during the test. Add 20 cc. of Wijs solution from a pipette, having a rather small delivery aperture. Close the bottle, place in a dark place, and note the time. It is convenient to keep the bottles during the test partly immersed in water which should be kept as nearly as possible between 22 and 23° C.

Pure shellac will scarcely alter the color of the Wijs solution. If in small amount, rosin will produce a slowly appearing red-brown color. In large amount, rosin causes an immediate coloration, increasing in intensity as time passes. After 1 hour, add 10 cc. of 10-per-cent potassium-iodide water solution. Titrate the solution immediately with the sodium-thiosulfate solution; 25 or 30 cc. may be run in immediately, unless the shellac is very impure, and the remainder gradually, with vigorous shaking. Just before the end, add a little starch solution. The end point is sharp, as the reaction products of shellac remain dissolved in the chloroform; any color returning after ½ minute or so is disregarded.

A blank determination should be run with 20 cc. of Wijs solution, 20 cc. of acetic acid, 10 cc. of chloroform, and 10 cc. of 10-per-cent potassium-iodide solution. The blank is necessary on account of the well-known effect of temperature changes on the volume, and possible loss of strength of the Wijs solution.

In the case of grossly adulterated samples, or in the testing of pure rosin, it is necessary to use, instead of 0.2 g. of material, a smaller amount, say 0.15 g. or even 0.1 g., in order that the excess of iodine monochloride may not be be too greatly reduced, since the excess of halogen is one of the factors in determining the amount of absorption. In case less than 25 cc. of the thiosulfate solution is required, another test should be made, using a smaller amount of the shellac to be tested.

In weighing shellac, some difficulty is at times experienced on account of its electrical properties. In very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it, and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

No pure shellacs show a higher iodine absorption than 18.* As shellac is relatively a high-priced material and as the variation between its highest

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* This statement has lately been questioned by one importer. Claim has been made for instance that even garnet-lac that is absolutely free of rosin may show a slightly higher iodine value than 18.

and lowest figure is not great, it is recommended that 18 should be taken as the standard figure for shellac, determined by the method above described.

As it is an accepted principle that a standard method should be so devised that its inaccuracies shall work in the direction of favoring the seller rather than of condemning too severely the article sold, it is recommended that the value for the iodine number of rosin be taken as 228. The result of using in this method the value 18 as the iodine number of shellac and 228 as the number of rosin, may be that a slightly lower percentage of rosin, under some circumstances, will be found than that which is actually present.

The percentage of rosin is determined as follows:

$$\begin{aligned}&\text{Iodine number of shellac} = 18\\&\text{Iodine number of rosin} = 228\\&\text{Iodine number of mixture} = X\\&\text{Percentage of rosin} = 100\frac{(X-18)}{(228-18)}\end{aligned}$$

On account of changes which take place from time to time in the effective strength of the Wijs solution on keeping, it is most desirable that there should be tested, side by side with the sample under examination, one or more samples of shellac of which the iodine number is known.

This effective strength is not completely indicated by its content of free halogen as measured by the thiosulfate solution.

ALCOHOL-INSOLUBLE MATTER

Dissolve 5 g. of the sample in a small beaker with 75 cc. of 99.5-per-cent methyl alcohol, by warming gradually on a steam bath until all the shellac is dissolved and the wax is in solution. Transfer this quickly into a weighed capsule (filter), previously wet with hot alcohol, putting the capsule into another small beaker which is immersed in hot water. A convenient apparatus to attain this result is a carbon filter tube of suitable size supported in a hot water bath, the outlet tube extending through the bottom of the bath allowing the escape of the filtrate. Wash all the residue from the first beaker in to the capsule with hot 99.5-per-cent methyl alcohol, and continue washing until the filtrate is practically colorless. Put the capsule in the extraction apparatus and extract for two hours. Dry to constant weight at 105° C.

The weight of the residue insoluble in the alcohol divided by the weight of the sample and this quotient multiplied by one hundred is the percentage of alcohol-insoluble matter in the lac.

DETERMINATION OF MOISTURE IN BLEACHED SHELLAC

Both orange and bleached shellac give off volatile matter at temperatures approaching 100° C. Bleached shellac alters chemically at these temperatures, losing its solubility in alcohol. For these reasons, the usual methods of determining moisture by heating in the air bath at 100 to 110° C. are not applicable in the analysis of shellac.

Sampling.—Bleached shellac is sold in three forms, as hanks or bars containing approximately 25 per cent of water, as ground bleached in pulverized form with about the same water content, and as bone-dry or kiln-dried shellac. The latter is prepared by drying the ground-bleached shellac in the air or in vacuum driers at moderate temperatures. It may contain, depending upon the completeness of the drying and weather conditions, up to 10 per cent or more of water.

In sampling bone-dry or kiln-dried bleached shellac, a fairly large portion (about 1 lb.) should be taken from different parts of the barrel and finely ground by running quickly through a coffee mill. No attempt shall be made to sieve it. It shall be rapidly mixed and transferred to a Mason jar provided with a screw cap and rubber ring seal. The jar should not be more than two-thirds full, leaving room for a thorough mixing by shaking the contents. It shall be kept in a cool place and tested as promptly as possible. If too warm the shellac may become partly caked, in which case the lumps shall be broken up by shaking the bottle.

In sampling bars or hanks it is recommended that a whole hank be taken. It should be crushed and ground as rapidly as possible. Ground-bleached shellac may be treated as above, bearing in mind that the large amount of moisture present makes rapid handling imperative.

Method No. 1.—Weigh from 5 to 10 g. of the sample in flat-bottom dishes about 4 in. in diameter or in watch glasses ground to fit and provided with a clamp. Spread out the contents of the dish in a thin layer to expose as large a surface as possible. Place the shellac in a desiccator freshly filled with concentrated sulfuric acid. Exhaust the desiccator by a vacuum pump as completely as possible. With a good vacuum (3 mm. pressure or better) constant weight will be obtained in between 24 and 48 hours.

Absolutely dry shellac is quite hygroscopic and the final weight should be taken as rapidly as possible.

Method No. 2.—The same results may be obtained by drying the shellac in a well-ventilated air bath from 3 to 6 hours at 100 to 110° F. (38 to 43° C.). One or two electric light bulbs provide a convenient source of heat. The temperature should not be allowed to rise above 43° C., otherwise sintering may occur and retard drying. With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight.

It is recommended that analysts check the accuracy of results obtained in the oven by comparison with a test made in a vacuum desiccator before relying exclusively on the oven.

Direct Method for Rosin.—A direct method for determining the amount of rosin in shellac has long been desired. Such a method is being worked out by the Bureau of Standards and promises to be very satisfactory. It is based upon the solubility of rosin in certain light fractions of petroleum hydrocarbons.

Other Shellac Constants.—The acid value of shellac may run from 60 to 66; the ash due to mineral matter from 0.6 to 20 % and the saponification value from 200 to 225, according to the grades. Further work may indicate the importance of including such constants in specifications.

Note.—When the determination of alcohol insoluble matter in bleached shellac is required, the sample shall be dried if in the form of bars or ground bleached, as the water present dilutes the alcohol to a point where solution may not be complete.

CHAPTER XXII.

EXAMINATION AND ANALYSIS OF VARNISH RESINS*

The value of a resin for varnish purposes depends largely upon its physical properties, such as color, hardness, and fusibility. In certain cases chemical tests such as acid number and acetyl value, yield important information. Knowledge of the chemistry of the varnish resins, however, is far from complete and their composition, except in two or three cases, is not definitely known. Consequently there is much confusion in the literature regarding the proper method of procedure for determining the chemical constants. The purchase of resins on chemical constants such as iodine, saponification, and acid values together with ash, color, and size of lumps may not be far distant. Such procedure would at least eliminate many fanciful "gradings" now existing and which have but little meaning.

PHYSICAL CHARACTERISTICS

Hardness.—The term hardness is purely relative, no definite method for determining it having yet been devised.† Moreover, the value of the resin depends not so much upon its initial hardness as upon the degree of hardness which it imparts to the finished varnish. A resin of greatest initial hardness, however, usually produces the hardest varnish. The general scale of hardness of the principal types of copal, according to E. J. Parry,‡ is as follows:

1. Zanzibar
2. Mozambique
3. Lindi
4. Benguela
5. Pebble
6. Sierra Leone (fossil)
7. Yellow Benguela
8. White Benguela
9. Camaroon
10. Congo
11. Manila
12. White Myola
13. Kauri
14. Sierra Leone (living trees)
15. South American

This table agrees fairly well with that of other investigators.

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* Arranged by P. C. Holdt.

† An ingenious method has been described by P. Nicolardot and Ch. Coffignier, Chimie et Industrie 5150-156-1921. In their apparatus a definite weight is applied to a small ball which rests on a piece of the resin. The relative hardness of a series of resins is inversely proportional to the diameter of the indentation observed when the weight is removed.

‡ Gums and Resins, E. J. Parry, Pitman & Sons, London.

Table XXV

Copals.	Alpha-dichlorhydrin.	Methyl-ethyl ketone.	Terpineol.	Carbon tetrachloride.	Chloral hydrate solution.	Ether followed by alcohol.	Mixture of equal parts CS_2 & C_6H_6.	Acetone.
White Angola...	About 25 p. c. dissolved.	About 10 p. c. dissolved.	Mostlydissolved, but with a gelatinous residue.	Insoluble.	....	Soluble to turbid liquid.	Almostentirely soluble.	Soluble to turbid liquid.
Red Angola.....	About 10 p. c. dissolved.	About 15 p. c. dissolved.	Mostly dissolved, but with a gelatinous residue.	Insoluble.	Almost insoluble [80 p. c.].	Soluble to turbid liquid.	Gelatinous without dissolving.	....
White Benguela.	About 10 p. c. dissolved.	About 15 p. c. dissolved.	Mostlydissolved, but with a gelatinous residue.	Insoluble.	Barely soluble [15 p. c.].	Partly soluble.	Barely soluble.	Soluble.
Yellow Benguela.	Almost insoluble.	About 20 p. c. dissolved.	Mostly dissolved, but with a gelatinous residue.	Insoluble.	Barely soluble [16 $\frac{2}{3}$ p. c.].	Partly soluble.	Gelatinous without dissolving.	Mostly soluble.
Congo.........	Partly dissolved.	About 10 p. c. dissolved.	Mostlydissolved, but with a gelatinous residue.	Insoluble.	Barely soluble [20 p. c.].	Slightly soluble.	Almost entirely soluble.	....
Sierra Leone....	Partly dissolved.	About 50 p. c. dissolved.	Most.y dissolved, but with a gelatinous residue.	Almost insoluble.	....	About 50 p. c. dissolved.	Barely soluble.	....
Cameroon......	Partly dissolved.	About 10 p. c. dissolved.	Gelatinous without dissolving.	About 25 p. c. dissolved	....	....	....	....
Zanzibar.......	Almost insoluble.	About 10 p. c. dissolved.	Mostly dissolved but with a gelatinous residue.	About 10 p. c. dissolved.	....	Soluble mostly after long digestion.	Barely soluble.	Partly soluble.
Brazil..........	Completely soluble.	Completely soluble.	Completely soluble.	Almost entirely soluble.	Barely soluble [30p. c.].	....	....	....
West Indies.....	Almost insoluble.	About 30 p. c. dissolved.	Mostly dissolved, but with a gelatinous residue	About 10 p. c. dissolved.	....	....	....	....
Kauri..........	Completely soluble.	Completely soluble.	Completely soluble.	About 10 p. c. dissolved.	Partly soluble [80 & 90 p. c.]	Almost entirely soluble.	Gelatinses.	Slightly soluble.
Manila.........	Completely soluble.	Almost entirely soluble.	Completely soluble.	Insoluble.	Mostly soluble [80 & 90 p. c.].	Entirely soluble.	Mostly soluble.	Gelatinises, a little dissolves.

The figures in brackets under chloral hydrate refer to the strength of the solution. This Table is due to Bottler.

According to Bottler, resins may be tested for hardness by scratching with rock salt. All are scratched; the hardest only with much difficulty. He classifies them in order of decreasing hardness:

1. Zanzibar
2. Red Angola
3. Sierra Leone
4. Benguela
5. Congo
6. Manila
7. White Angola
8. Kauri

Solubility.—The solubility of the various resins in different organic solvents has been thoroughly studied and numerous attempts made to develop a system of classification based on this property. The solubility of a particular resin varies with its age, handling after collection, etc. The hardest and best varieties are in general the most difficult soluble. Table XXV, XXVI and XXVII are taken from K. Dieterich's "Analysis of Resins."

TABLE XXVI—*Table Showing Percentage of Resins Dissolved by Various Solvents. By Coffignier*

	Ethyl Alcohol.	Ether.	Amyl Alcohol.	Spirits of Turpentine.	Carbon Tetra-chloride.
Zanzibar	14.10	25.00	36.70	Insoluble	Insoluble
Madagascar	26.20	35.00	77.60	39.70	15.00
Demerara	27.90	44.60	47.00	7.50	24.50
Congo	74.70	51.70	97.80	31.80	30.90
Sierra Leone	37.70	52.20	95.20	28.60	29.10
Brazil	69.80	70.30	98.20	51.80	55.10
Benguela	83.50	56.30	99.10	31.20	26.00
Kissel	42.60	57.40	91.50	20.40	30.10
Kamerun	33.30	44.20	70.80	21.40	26.30
Accra	52.20	56.00	95.90	20.30	19.70
Kauri, blond	93.40	38.20	Soluble	22.50	18.90
Kauri, brown	64.20	39.30	Soluble	26.40	22.70
Kauri, bush	87.70	52.70	Soluble	27.10	28.10
Manila, hard	44.10	41.50	Soluble	26.80	31.00
Manila, friable	Soluble	71.30	Soluble	35.90	38.00
Pontianac	Soluble	54.00	Soluble	33.60	38.09
Blue Angola	84.90	72.70	98.60	30.60	38.70
Red Angola	62.40	48.70	93.00	23.00	22.30
Colombia	83.00	50.00	95.10	31.30	30.40

Fusibility.—None of the resins have sharply defined melting points. The fusing is a continuous process and may extend over a considerable range of temperature, as indicated in the table below. The harder resins require higher temperatures to melt them, and always undergo partial decomposition during the melting process. Different samples of the same kind of resin often differ considerably in this respect, hence the melting point is of little value in identifying a resin.

TABLE XXVII—*Due to Coffignier*

	Specific Gravity.	Softening Point.	Melting Point.
Benguela	1.058 at 16°	65°	165°
Angola (white)	1.055 at 17°	45°	95°
Angola (red)	1.066 at 17°	90°	300°
Congo	1.061 at 17°	90°	195°
Sierra Leone	1.072 at 19°	60°	130°
Kissel	1.066 at 27°	....	110°
Cameroon	1.052 at 27°	....	150°
Accra	1.033 at 27°	....	120°
Manila (hard)	1.065 at 17°	80°	190°
Manila (friable)	1.060 at 17°	45°	120°
Pontianak	1.037 at 16°	55°	135°
Brazil	....	....	100°
Colombia	....	....	above 300

Specific Gravity.—According to Bottler and Sabin,* specific gravity determinations are very useful in estimating the value of a resin. The specific gravity of the resin in its usual condition and after being freed from contained air is found. The resins showing the smallest differences contain the least enclosed air and are assumed to be more valuable than their opposites. They find that Zanzibar, thus treated at 15° C., gives 1.0621 and 1.0636, the difference being 0.0015. Lindi copal shows a difference of 0.0010; red Angola 0.014; Camaroon 0.015; Manila 0.059; and Kauri 0.064.

A method for specific gravity suggested by Dieterich for rosin and which could be applied to other resins is as follows:

A series of solutions of common salt, ranging between sp. gr. 1.070 and 1.085 at 15° C., are prepared, and in each of these is placed a few fragments of the colophony under examination, the temperature being maintained constant. The sp. gr. of the solution which retains the colophony in suspension will be the same as that of the substance. In selecting the test pieces, care must be taken to reject any which exhibit cracks, air bubbles, or impurities.

CHEMICAL EXAMINATION

Tschirch and his collaborators, K. Dieterich and others, have done a great deal of work on the various resins and have col-

* Bottler & Sabin, German & American Varnish making, John Wiley & Sons. Pages 13-14.

lected much data concerning their composition, and chemical behavior. According to the majority of investigators, varnish resins consist largely of resin acids (resinolic acids) and neutral substances of unknown composition (designated resenes by Tschirch), with small proportions of volatile compounds, ash and impurities. The absence of esters, ethers, anhydrides and lactones (except in the case of rosin) has been fairly well established.*

According to Tschirch and Stephen, the composition of Zanzibar copal is as follows: trachylolic acid ($C_{56}H_{58}O_8$), 80 per cent; iso-trachylolic acid ($C_{56}H_{88}O_8$), 4 per cent; essential oil, 9.46 per cent; Alpha-resene ($C_{41}H_{68}O_4$) and Beta-resene ($C_{25}H_{38}O_4$), together 6 per cent; ash .12 per cent; impurities .42 per cent. Congo copal, according to A. Engel† has the following composition: Congo Copalic Acid ($C_{19}H_{30}O_2$) 48 to 50 per cent; Congo-Copalolic Acid ($C_{22}H_{34}O_4$) 22 per cent; Alpha Congo-Copal Resene, 5 to 6 per cent; Beta Congo Copal Resene, 12 per cent; Ethereal Oil, 3 to 4 per cent; Impurities and Ash, 4 to 5 per cent.

For those resins which contain no other saponifiable compounds than the free resin acids, it might be expected that the acid number, determined in the usual manner (i. e., by dissolving the resin in a suitable solvent and titrating directly with KOH solution) would be identical with the saponification number. This, however, is not found to be true in practice. The saponification number (indirect acid number) is usually considerably higher than the direct acid number. There are probably several contributing causes for this variation. According to evidence presented by Worstall,‡ (in a very excellent article on Fossil Resins) when a resin is titrated directly with an alkali solution, the resin acids are neutralized very slowly. There are also indications that small amounts of aldehydes may be present and that these take up alkali during the saponification process, thus giving a higher figure by this method.

Numerous methods have been proposed for determining acid and saponification numbers using different solvents in varying proportions. Widely varying values have been reported, and much of the literature on the subject is highly contradictory.

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* E. J. Parry, contrary to most other workers, states that all copals contain esters.

† Journal American Chemical Society, 1903; Vol. 25, Page 860.

‡ *Archive der Pharmacil,* 1908, Page 293.

These differences of opinion are undoubtedly due in some cases to actual variations in the samples examined, many being of doubtful origin. In other cases where there is a wide divergence on apparently authentic samples of the same resin, it is probably due largely to a difference in the method employed. Hence reported values are meaningless unless the method used is specifically described.

Since many of the resins are insoluble or only partially soluble in alcohol, it is in general advisable to use other solvents. Various mixtures of alcohol, benzine, benzol, ether and chloroform have been suggested. Alcohol alone is suitable only for rosin, shellac, and possibly Manila.

The presence of water in the solution should be carefully avoided. It will not mix with most organic solvents, but forms an emulsion which makes the titration more difficult by rendering the end point less distinct. Furthermore, according to Dieterich, the addition of water decomposes the resin soaps and results in abnormally high values. An alcoholic KOH solution should always be employed.

Direct Acid Value.—(Applicable only to rosin, shellac and possibly one or two other resins.) From one to three grams of the resin is dissolved in about 50 cc. of the solvent in an Erlenmeyer flask. (Alcohol alone is a suitable solvent for rosin and shellac; for all others a mixture of equal parts of alcohol and benzol should be used.) The mixture is boiled gently for ½ hour under a reflux condenser, cooled and titrated with tenth or fifth normal alcoholic KOH. Or the mixture may be allowed to stand over night and then titrated without subjecting it to any heating. Use phenol-phthalein as indicator.

Saponification Value.—(Indirect acid value for fossil resins and all others containing no other saponifiable matter than the resin acids.) An excellent method was recommended by K. Dieterich. Worstall * used the same method with a slight modification in solvents. His method was as follows:

Weigh one gram of the finely powdered resin into a glass-stoppered bottle and add 15 cc. benzol and 5 cc. alcohol. Solution is complete in a few minutes with these solvents. Then add 15 cc. fifth normal alcoholic potash solution and allow to stand 18 hours. Add 25 cc. alcohol and titrate the excess alkali with fifth normal sulphuric acid, using phenolphthalein as the indicator. Blank determinations are run each time. The addition

* *Journal American Chemical Society,* Vol. 25, 1903; Page 862.

of alcohol before the titration is a great help in securing sharp end reactions.

Acetyl Value.—K. Dieterich proposed the following method for determining the acetyl value of resins:

"Boil the resin under a reflux condenser with an excess of acetic anhydride and a little anhydrous sodium acetate, until completely dissolved, or until it is evident that no further portion will pass into solution. Pour the solution into water, collect the ensuing precipitate and extract with boiling water until perfectly free from all traces of uncombined acetic acid. The insoluble residues left by copal and dammar are also treated in the same manner. The dried acetylized products are then tested for the acetyl, acid, ester and saponification values by dissolving 1 gram in cold alcohol and titrating with half normal caustic potash. The saponification is also effected with half normal alkali for half an hour under a reflux condenser, and the product titrated back after cooling and dilution with alcohol (not water). As in the case of fats, the difference between the acetyl-saponification value and the acetyl-acid value gives the 'true acetyl value.'"

CHAPTER XXIII.

EXAMINATION OF TURPENTINE AND MINERAL SPIRITS

Evaporative Value.—Physical and chemical methods for the examination of turpentine and mineral spirits are given in the specifications of the Interdepartmental Committee, that are bound in the back of this volume. With mineral spirits, less uniform grading is found in commercial practice than with turpentine. For this reason manufacturers of paint and varnish often experience considerable difficulty in securing uniform and standard types of mineral spirits for their work. Therefore, in addition to the tests prescribed in the specifications referred to, it is well for the chemist to make a study of the evaporative value of various grades of mineral spirits submitted. For this purpose a good exterior and a good interior varnish base may be selected, heated, and thinned with about an equal quantity by weight of mineral spirits of the grades being tested. The varnishes may then be applied to weighed glass plates which should be re-weighed every fifteen minutes for a period of two hours. The loss in volatile is then reported. (See Circular No. 141 of the Scientific Section.) Mineral spirits having large quantities of heavy, non-volatile ends will readily be noticed. The body of the varnishes and the brushing, flowing and leveling properties should also be ascertained by further tests.

Solvent Properties.—It is also advisable to make a test to determine the solvent properties of the mineral spirits, and for this purpose it is customary to use varnish bases as referred to above, thinning down with equal parts by weight of the mineral spirits being tested. The reduced samples are generally placed in 4 oz. oil bottles and inspected for a period of 10 to 12 days to watch for the development of suspended matter, turbidity or other precipitated products due to lack of solvent properties of the thinner. Distillation of a sample of the mineral spirits and examination of the various fractions for solvent properties often gives much information of value.

One of the most useful materials to include in a test for the solvent character of mineral spirits is extremely heavy-bodied linseed oil. Apparent solution takes place when such an oil is

thinned with mineral spirits, but after standing, the oil is often thrown out, showing that the preliminary solution was only of a suspension colloid type. The continued addition of increments of mineral spirits to a volume of heavy-bodied oil, until the precipitation point is reached, will give relative data of almost quantitative character. Since such oils are often used in flat finishes which sometimes contain in the liquid portion as high as 75 per cent of mineral spirits, the throwing out of the oil would be a very objectionable feature.

There appears to be a great difference in the action of the various brands of mineral spirits with bodied oils, especially blown oils. Turpentine usually mixes well in all proportions

TABLE XXVIII

Thinner.	Begins to cloud.		Separation occurs.	
	Oil.	Thinner.	Oil.	Thinner.
D	1	2	1	3
E	1	8	1	8
F	No cloudiness or separation at any dilution.			
G	1	10	1	11
I	No cloudiness or separation at any dilution.			
J	1	3	1	4
K	1	3	1	4
L	1	8	1	10

with such oils. When equal portions of the same oil and mineral spirits are mixed, some samples show a turbid and milky appearance. As the quantity of thinner is increased the turbidity increases until separation occurs. While in some grades cloudiness occurs even at low dilution, other samples may not become turbid until much greater dilutions have been reached. Some may remain clear when mixed in practically any proportion. Where there is only a slight turbidity at first, complete separation may occur on standing. The accompanying chart shows the dilutions at which cloudiness and oil separation first occurred when thinning a very heavy grade of blown and heat-treated linseed oil with several commercial grades of mineral spirits. Figures indicate parts by weight.

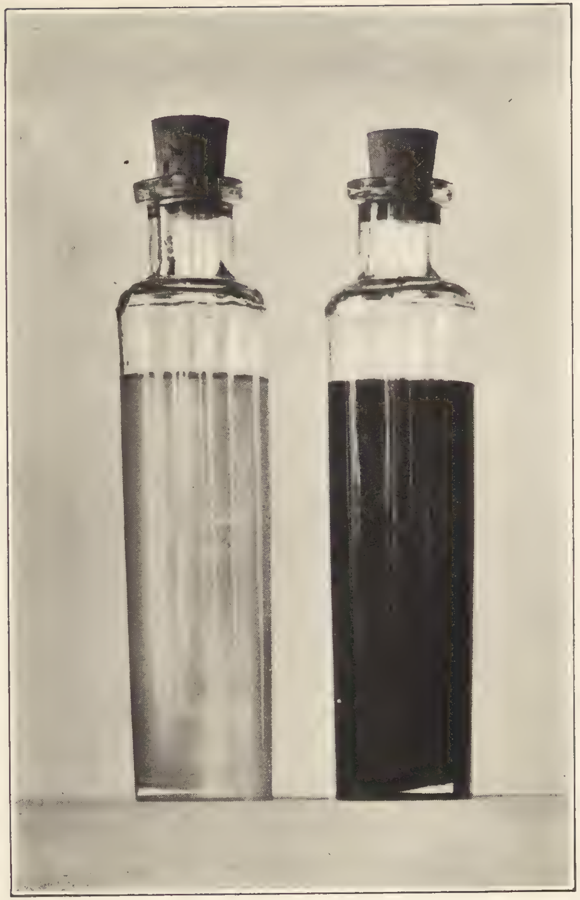

FIG. 48—Two samples of the same varnish thinned with different grades of mineral spirits. Note dark color of one caused by reaction between the sulphur content of the mineral spirits and the dissolved lead drier in the varnish.

FIG. 49—Flat paint liquid thinned with grade of thinner that has caused separation of the bodied oil.

F J D

FIG. 50—Ten gram samples of heavy bodied linseed oil placed in each bottle. A different grade of mineral spirits added to each. When cloudiness was shown, addition of mineral spirits discontinued. Only small quantity required to cloud and throw out oil in test D. Considerable required to cloud test J. Test F shows no cloudiness and is miscible with oil at all dilutions.

In making these dilution tests a tall narrow beaker may be conveniently used. A fair idea of the miscibility of the thinner may be obtained in the following manner: Weigh out a small quantity of bodied oil, say 5 or 10 grams, in the beaker. Then add an equal quantity of the mineral spirits to be tested. Stir with a glass rod, noting the readiness with which the two layers mix. Some samples will show a cloudiness at once, which may, however, disappear as the two mix. Others may mix perfectly clear. Add successive portions of the thinner, stirring after each addition and noting carefully the appearance, readiness of mixing, etc. Determine the point at which a permanent milkiness results. After the addition of one or two more portions, part or all of the oil will usually separate on standing a short time.

While the quantity of thinner required to throw out the oil may in many cases be far in excess of the proportion ordinarily used, yet in consideration of the fact that the products which exhibit the greatest tendency to become turbid are most likely to separate on standing, it seems advisable to employ only those which stand up best under the dilution test.

Whether the thinner is derived from an asphaltum base or paraffin base petroleum is of little importance so long as it conforms to other requirements (see Circular No. 94). The asphaltum base petroleums are said to possess in general, greater solvent power, due to the presence of a larger proportion of cyclic hydrocarbons. If desired, the proportion of the latter may be estimated comparatively by the Formolit Reaction (Nastjukoff Test).* But practical tests, such as those described herein, must remain the deciding ones in determining the value of a given thinner.

Sulphur Content.—Another very important observation to be made on mineral spirits is the effect of the sulphur content upon the color of paints or varnishes in which they are used. The white lead test that has in the past been used for this purpose will not very often disclose the presence of objectionable sulphur compounds. The Doctor test is not sensitive and is rather difficult to perform. Varnishes, however, which contain metallic driers, such as lead, in organic solution, will rapidly become darkened when thinned with mineral spirits containing certain objectionable sulphur compounds. Some grades of mineral

* See Holde-Mueller, Examination of Hydrocarbon Oils and Saponifiable Fats, John Wiley & Sons, p. 38.

spirits, for instance, may contain as high as 1½ per cent of sulphur. If this sulphur is in a certain fixed form, it may not darken with lead compounds in solution. Other grades of mineral spirits, which contain even very small traces of sulphur in readily available form, will quickly darken organic lead solutions. One test which the writer has used is as follows:

Make up a varnish base by fusing 100 grams of rosin with five-tenths of a gram of lead oxide. If desired, cobalt, manganese, copper and other oxides that are liable to be present in a cooked varnish, may also be included in small amounts. This is then used as the base for test. 100 grams of the product is heated and thinned down with 100 grams of the mineral spirits to be tested, and held at a temperature of about 350° F. for 30 minutes, preferably in a reflux condenser. Darkening will occur with those grades of mineral spirits having reactionable sulphur content.

Probably the most graphic test for sulphur in mineral spirits is the copper strip test. This is made by placing in a carbon tube about 15″ long and ½″ in width, a strip of copper ¼″ wide and 2″ long. Sufficient mineral spirits is added to completely cover the copper. The tube is then immersed in an oil bath which is run up to 350° F. or to such temperature as will cause the mineral spirits to boil. The test should be run for a period of 30 minutes, and the effect on the copper strip observed. If only a slight bloom or fluorescence is shown, the mineral spirits should be acceptable. If blackening of the strip is shown, the mineral spirits should be looked upon as unsatisfactory for certain varnishes. This test will show a blackened condition of copper if the mineral spirits contains even .04 per cent of reactive sulphur.

CHAPTER XXIV.

BITUMINOUS PAINTS, VARNISHES, CEMENTS AND SIMILAR MATERIALS.

During the past five years the use of bituminous substances for cold application as protective coatings has increased considerably. This has resulted in an urgent demand for specifications and methods for analyzing and testing them. Heretofore, reliable methods have not been available. The following descriptions and methods, as prepared for this volume by E. F. Berger of the Bureau of Standards, are to be highly recommended.

Bituminous compositions for cold application can be divided into paints, coatings, varnishes, japans, and plastic cements.

Bituminous Paints.—Bituminous paints are generally mixtures of a bituminous material and a volatile solvent which are of brushing consistency and which dry and harden by the evaporation of the volatile solvent. They may contain mineral filler and pigment and small amounts of fatty matter. The term, paint, as defined by the A. S. T. M. is, however, misapplied to these materials except in the few instances where pigment is added.

Bituminous paints are marketed under various names but the most important kinds can be classed as dampproofing and roofing paints. Dampproofing paints are used almost exclusively on masonry and concrete to prevent the absorption or penetration of moisture and are rarely exposed to the weather, being protected in some manner. The two most common kinds are stone backing and plaster bond.

Stone backing is a solution of a bituminous material in a volatile solvent used for coating all surfaces except the exposed face of cut stone, concrete blocks, etc., to prevent staining, efflorescence, or other discoloration of the exposed face. It is of heavy brushing consistency, invariably dries to a tough, flexible film free from tackiness and which will not chip or flake off in handling. They are composed either of asphaltic or coal tar materials.

Plaster bond is a solution of a rather soft bituminous substance in a suitable volatile solvent for coating the inside of exterior walls of brick, tile, stone, etc., before plastering to

prevent staining, etc. Its value as a means of increasing the bond between the plaster and the wall is a matter of question. Plaster bonds are usually made from asphaltic materials and may contain fatty materials, rosin, rosin oil, aluminum stearate or oleate or other heavy metal soaps. They are of heavier consistency than stone backings and dry to soft, flexible films which have a tendency to remain permanently tacky or sticky.

Roofing paints are used for painting metal roofs and for recoating prepared and built-up bituminous roofing. They vary in consistency from those which can be applied with an ordinary paint brush to those which require a stiff bristle dauber or three knot roof brush for application. The former are usually called roofing paints and the latter roof coatings. Roofing paints consist of a bituminous material thinned with a solvent and may contain fine mineral filler or pigments. When pigments are present, some drying or fatty oil may be used. Roof coatings are of heavier consistency than roof paints and contain mineral or other filler usually of a fibrous character in the proportion of about 5 to 15 parts per 100 parts of finished paint. Their common trade name is liquid fibrous asbestos roof coating. Roof paints and coatings may be made from either asphaltic or coal tar materials. When using them for prepared or built-up roofing only asphaltic materials should be applied over asphaltic roofings and only coal tar materials over roofings made with coal tar materials.

Occasionally paints are encountered which consist of a bituminous substance dissolved in carbon bisulphide or carbon tetrachloride. These paints are based on the formula given in the patent of Pearce & Beardsley. Their chief advantage is that they dry rapidly and give relatively thicker dried films than paints of the same consistency made with ordinary solvents.

Bituminous Varnishes.—Bituminous varnishes are mixtures of a bituminous material and fatty oil thinned to a suitable consistency with a volatile solvent which dry partially by the evaporation of the volatile solvent and partially by the oxidation of the fatty oil. The toughness and general characteristics of the film obtained from bituminous varnishes are influenced by the fatty oil present. Bituminous varnishes may be either long or short oil but those most commonly sold are the short oil type with about one part of oil to four of bituminous material. Hard bituminous materials are generally used and include gilsonite,

hard native and residual oil asphalts, glance pitch, manjak, wurtzelite pitch, grahamite, and fatty acid pitches.

Bituminous Japans.—Bituminous japans are mixtures of bituminous materials with or without fatty oil and resins and volatile solvent, the drying and hardening of which is brought about by baking. The cheaper grades of japan usually consist of a bituminous substance dissolved in a solvent, the better grades are mixtures of a bituminous substance with fatty acid pitch, drying oils, and resins, with or without small amounts of pigment. Most black insulating varnishes and Brunswick Black are of this character.

Bituminous Plastic Cements.—Bituminous plastic cements are mixtures of trowelling consistency of bituminous materials with or without fatty oil and volatile solvent and containing about 15 to 40 parts of filler, generally of a fibrous character, per 100 parts of cement. They are applied in thick layers and usually dry to tough coatings which remain plastic for long periods. They are made either from asphaltic or coal tar materials and the same precautions should be taken in their use on bituminous roofing as with roof paints and coatings. Pine tar, pine tar oil, and hard wood tar are sometimes used to improve spreading quality and to modify the odor of coal tar materials.

CONSTITUENTS OF BITUMINOUS PAINTS, VARNISHES, CEMENTS, ETC.

The following materials are generally used in these products, although any material entering into the manufacture of oil paints, varnishes, etc., is likely to be used.

(1) *Bituminous Materials.*

Petroleum Asphalts	Glance Pitch
Trinidad Asphalt	Wurtzelite Pitch
Bermudez Asphalt	Coal Tar Pitch
Gilsonite	Water Gas Tar Pitch
Grahamite	Pine Tar and Wood Pitches
Manjak	Fatty Acid Pitches

(2) *Fatty and Resinous Materials.*

Linseed Oil	Castor Oil
China Wood Oil	Rosin
Cottonseed Oil	Fossil Resins
Rosin Oil	

(3) *Driers.*

Any drier used in oil paints and varnishes.

(4) *Thinners.*

Petroleum Distillates	Pine Oil and Pine Tar Oil
Coal Tar Distillates	Carbon Bisulphide
Turpentine	Carbon Tetrachloride

(5) *Fillers and Pigments.*

Asbestos	Slate Dust
Asbestine	Silica
Clay	Rag Fibers
Portland Cement	Jute Fibers
Limestone Dust	Paper Pulp
Gypsum	

METHODS OF ANALYSIS AND TEST

(A) *Volatile and Nonvolatile:*

(1) *Materials without filler.*—Heat a 1.5 to 2 gram sample in a tared metal dish at 105° to 110°C. for three hours. The loss in weight is calculated as volatile.

(2) *Materials with filler.*—Heat a 3 to 5 gram sample spread out to a thin layer in a tared metal dish at 105° to 110°C. for seven hours. The loss in weight is calculated as volatile.

(B) *Separation and Examination of Thinner:*

(1) *Low boiling thinners.*—Distill 100 grams of the sample with steam at a temperature of 130°C., collecting the distillate in a separatory funnel. Stop the distillation when 300 cc. of water has distilled. When the distillate has separated into two distinct layers, draw off the water, and examine the distillate for refractive index, specific gravity, soluble in 38 N. sulphuric acid, dimethyl sulphate, or by any other tests necessary for its identification. If no pigment or filler is present the residue in the flask may be dried and used for further testing as in paragraph (D).

(2) *High boiling thinners.*—Distill 100 grams of the sample in a 200 cc. Engler distilling flask at the rate of about one drop per second, avoiding overheating, which may crack the bituminous material. Collect fractions up to 170°C., and 170° to 300°C., at which point the distillation is stopped. In most cases the thinner will all have distilled at a point below 300°C. and the distillation should be stopped when this occurs. The distillates are examined as in (1). The residue in the flask is allowed to cool until vapors are no longer evolved, when it is poured out

into a suitable container and, if no pigments are present, preserved for further testing as in paragraph (D).

(C) *Fillers, Pigments and Free Carbon:*

Separate the fillers, pigments, and free carbon from the vehicle by any of the following methods:

(1) Weigh accurately about 10 grams of the sample into a centrifuge tube. Add about 25 cc. of benzol and stir so as to break up the sample, then add about 25 cc. more solvent and centrifuge until well settled. Decant the supernatant liquid and repeat the extraction twice with 50 cc. portions of benzol and then with a mixture of equal parts of benzol and carbon tetrachloride until the supernatant liquid is colorless. Dry residue in tube at 105° to 110°C. for one hour and weigh. Preserve extracts for further examination of vehicle. The insoluble residue contains the pigment and fillers, and mineral matter occurring naturally in the bituminous materials (i. e., Trinidad and Bermudez asphalts) and free carbon from coal tar pitches.

(2) Weigh accurately about 5 grams of the sample into a small beaker, add 25 cc. of carbon bisulphide or carbon tetrachloride or benzol (if an examination of the vehicle is to be made), break up the sample by stirring and allow to stand for 15 minutes. Filter through a weighed Gooch crucible, prepared with a medium thick mat of asbestos, or an Alundum crucible using suction if necessary to aid filtration. Wash the residue in the crucible until the washings are colorless, dry in air at room temperature until the odor of carbon bisulphide has almost disappeared, and then for 1 hour at 105° to 110°C. Cool, weigh, and calculate percentage of insoluble material. In this method if Trinidad asphalt is present some of the fine mineral matter may pass through into the extract. This can be determined by evaporating the extract, burning off the bituminous matter, and weighing the ash obtained.

(3) Weigh the sample into a paper thimble and extract in a Soxhlet or other suitable extractor.

Examination of insoluble matter.—The insoluble matter (filler, pigment, free carbon) is examined as in the case of oil paints, except as follows:

(1) *Fibrous Filler.*—Examine microscopically for mineral wool, rag fibers, jute, paper pulp and asbestos.

(2) *Free carbon from coal tar compositions, in presence of mineral matter containing water of crystallization.*—When the filler is asbestos, this method gives satisfactory results. Extract

about 5 grams of the sample as in "C" and weigh the residue of carbon and asbestos. Now burn off the carbon and weigh. Increase this weight by 14 per cent to compensate for water of crystallization driven off from the asbestos. Calculate percentages of free carbon and asbestos.

(3) *For mixtures of free carbon with asbestos and clay.*—The following method has been suggested but has not as yet been thoroughly investigated: Extract about 5 grams of the sample as in "C" and weigh the residue. Ignite the residue in a crucible for seven minutes in a current of dry carbon dioxide (using a Rose crucible cover) with a flame about 20 cm. high, or in a platinum crucible with a tightly fitting cover in a muffle at between 950° and 975°C. for seven minutes. Cool and weigh. The loss in weight is water of crystallization from the filler. Now burn off the carbon, cool, weigh and calculate the loss in weight as free carbon.

(D) *Nonvolatile Vehicle:*

Saponifiable or fatty matter may be determined by either of the following methods. If no pigment or filler is present, the original material may be taken. If pigment or filler is present, it should be removed as in (C) and the extract containing the nonvolatile vehicle or base should be evaporated to a small volume over a steam bath.

(1) The following method is essentially that given in "Asphalts and Allied Substances"—1920, by Herbert Abraham.

Weigh 5 grams of the original material (or take the evaporated extract from 7.5 grams of material obtained as in (C)) and dissolve in 50 cc. of benzol using heat, if necessary, to aid solution. Add 5 cc. of dilute nitric acid (1: 1) and boil under a reflux condenser for one-half hour to decompose any metallic soaps (i. e., driers, etc.). Add 150 cc. of water, boil under a reflux condenser, then transfer to a separatory funnel, draw off the aqueous layer, and repeat extractions with water until all metals are removed.

To the benzol solution add 30 cc. of a saponifying liquid made by dissolving 100 grams of anhydrous potassium hydroxide in 500 cc. of 95 per cent ethyl alcohol and diluting to 1,000 cc. with 90 per cent benzol, and boil under a reflux condenser from one-half to one hour.

Pour the mixture while still warm into a separatory funnel containing 150 cc. of boiling water and 25 cc. of a 10 per cent solution of potassium chloride. Add 250 cc. of benzol, shake

vigorously, and allow the funnel to rest quietly in a warm place until the solvent separates. (If an emulsion forms which refuses to separate on standing, add 200 cc. of benzol and 100 cc. of 95 per cent ethyl alcohol and stand in a warm place over night.) Usually three layers are obtained. Draw off the aqueous solution of the soaps as completely as possible and decant the benzol layer leaving the intermediate layer in the funnel.

Extract the aqueous soap solution with 200 cc. portions of benzol until the benzol extract is colorless.

Combine the benzol extracts with the layer obtained from the funnel and extract with 100 cc. portions of 50 per cent ethyl alcohol. Add the alcohol extracts of the benzol layer to the intermediate layer in the separatory funnel and extract with benzol until the benzol extracts are colorless.

Combine the benzol extracts, evaporate, dry at 105°C., and weigh as unsaponifiable.

Combine the aqueous soap and alcohol extracts and acidify with dilute hydrochloric acid, warm, and extract with benzol. Evaporate the benzol extract, dry at 100°C. and weigh as saponifiable.

(2) The following method (B. S. Circular 104, Recommended Specifications for Asphalt Varnish) is more rapid and avoids troublesome emulsions. It has not been tried on compositions containing very soft petroleum asphalts, Trinidad and Bermudez asphalt, or resins, but it gives satisfactory results on mixtures of fatty oil with hard petroleum asphalts, gilsonite, wurtzelite pitch, and manjak.

Weigh about 5 grams of the material into a wide-mouthed flask (or take the evaporated extract from 7.5 grams of material obtained as in (C)), add 50 cc. of benzol and 5 grams of silica sand, and heat under a reflux condenser on a steam bath until the material is entirely dissolved. Add 25 cc. of a half normal alcoholic caustic potash solution, and 25 cc. of denatured alcohol, and continue boiling under the reflux condenser for one hour. Remove the condenser and evaporate the solution to dryness.

Add to the residue in the flask 50 cc. of distilled water and heat until the residue is disintegrated. Filter the water solution of the soaps. Repeat this operation with 25 cc. portions of water until the residue is completely disintegrated and the wash water is clear and colorless.

Combine the filtrates (the soap solution and washings), acidify with hydrochloric acid, and heat until the fatty acids and any

emulsified asphalt separate and rise to the top, and the water below is clear.

Cool, transfer to a separatory funnel, and extract three times with 50 cc. portions of ether. Combine the ether extracts and wash with water until free from acid. Filter the ether extracts through paper into a beaker and wash the residue on the paper with ether until the washing runs through colorless. Evaporate the ether solutions to dryness.

Add 15 cc. of 95 per cent ethyl alcohol to the residue in the beaker and warm on the steam bath. Cool to room temperature and filter through paper into a tared flask or dish. Repeat this operation with 10 cc. portions of 95 per cent ethyl alcohol until the alcohol remains colorless. Finally wash the residue on the paper with 95 per cent ethyl alcohol until the washings run through colorless.

Evaporate to dryness on a steam bath and heat for an hour in an oven at 105°C. (221°F.). Cool and weigh. From the weight of the residue in the flask and the weight of the original sample calculate the percentage of fatty matter.

(Sometimes the residue obtained after saponification and the evaporation of the benzol and alcohol from the saponifying mixture is not completely disintegrated by boiling with water. In that case, extract with water until nothing further dissolves and then dry. Dissolve in benzol, using heat if necessary, and wash the benzol solution several times with water. Heat the washings until the odor of benzol has disappeared and add to the soap solution before acidifying.)

Examination of Saponifiable.—The saponifiable obtained as above may be separated into fatty and resin acids by method of E. W. Boughton, B. S. Tech. Paper No. 65, and may be tested for rosin and fatty acid pitch (Test 37b) "Asphalt and Allied Substances" by Herbert Abraham—1920.

Examination of Unsaponifiable.—The unsaponifiable should be tested for melting point and fixed carbon. In case the sample contains no pigment, filler, or saponifiable these tests should be made on the nonvolatile obtained as in (A) or in the residue from distillation as in (B).

For asphaltic materials determine the melting point by the "Standard Method of Test for Softening Point of Bituminous Materials Other Than Tar Products"—D. 36-21, A. S. T. M. Standards, 1921, page 739—(Ring and Ball Method).

For tar products determine the melting point by the "Standard Method of Test for Softening Point of Tar Products"—D. 61-20, A. S. T. M. Standards, 1921, page 743—(Cube in Water Method).

For tar products having melting points above 77°C. (170.6°F.) use Cube Method in Air—"Asphalts and Allied Substances," by Herbert Abraham—1920, page 516.

Determine fixed carbon on asphaltic materials by method given in Journal of American Chemical Society, 1899, Vol. 21, page 1116, or "Fixed Carbon in Bituminous Materials, Its Determination and Value in Specifications," by L. Kirschbaum, Eng. Contr. *39*, 172 (1913). The fixed carbon obtained from common asphaltic materials is as follows:

Bermudez Asphalt	12	to 14 per cent
California Asphalt	9½	to 18 per cent
Mexican Asphalt	15	to 22 per cent
Texas Asphalt	13	to 16 per cent
Trinidad Asphalt	10	to 13 per cent
Gilsonite	14	to 20 per cent
Wurtzelite Pitch	15	to 25 per cent
Grahamite	30	to 55 per cent

(E) *Tests for the Differentiation of Asphalt and Coal Tar Pitch:*

Owing to the prejudice of the buying public against coal tar paints and cements, brought about by the use of materials of poor quality made from coal tar materials, and the fact that some dealers in asphaltic materials are using these failures as selling arguments, the analyst is often called upon to prove the presence of coal tar materials other than thinners in asphaltic products and vice versa.

The following tests are useful for this purpose:

(1) *Color of solution of nonvolatile in benzol.*—Coal tar materials usually give a solution with a yellowish or greenish brown fluorescence. Asphaltic materials give a brown solution without flourescence. The presence of oily constituents in some asphalts may at times give a flourescence that might be mistaken for that obtained from coal tar materials. Wood pitches may also give a slight flourescence.

(2) *Free Carbon.*—The presence of free carbon indicates the presence of coal tar or coal tar pitch.

(3) *Distillation Test.*—Weigh into an iron or copper distilling retort 100 grams of the material under examination. Heat

very slowly until distillation begins and then distill off the thinner at the rate of about one drop a second. Usually around 200°C. a point will be reached where the distillate will stop coming over and the temperature will tend to drop. At this point the thinner is usually all removed. Change the receiver and continue distillation so as to crack or destructively distill the bituminous material until the temperature reaches 360°C. Note the character of the distillate. Asphaltic materials usually give liquid distillates of a brown or reddish brown color. Coal tar materials usually give solid distillates of orange or reddish color or liquid distillates from which crystals tend to separate. The character of distillates from mixtures of the two materials varies. The presence of fatty oil is recognized by the odor of acrolein.

The following tests are made on the cracked distillate:

(a) *Specific Gravity of Cracked Distillate at 25°C.*—Cracked distillate of asphaltic materials—0.74 to 0.87. Coal tar materials—0.98 to 1.07. Cracked fatty oil lowers the specific gravity.

(b) *Sulphonation with 38 N H_2SO_4.*

The following amounts of residue are usually obtained:

Coal Tar Materials	0 to 10 per cent
Water Gas Tar Pitch	0 to 15 per cent
Asphaltic Materials	min. 80 per cent
Wood Tar Pitches	0 to 5 per cent
Fatty Acid Pitches and Fatty Oils	0 to 5 per cent

(c) *Soluble in Dimethyl Sulphate.*—This test may be used but with caution owing to its unreliability in the case of small amounts of either material.

The distillates from coal tar materials are usually completely soluble in dimethyl sulphate, while those from asphaltic materials are about 85 per cent insoluble.

(d) *Anthraquinone Test.*—Melt the distillate if solid or if it contains solid particles and take about 5 cc. for examination. Cool and add 10 cc. of absolute ethyl alcohol and allow to stand until the solids separate. Decant the liquid and dry the solids. Dissolve in 45 cc. of glacial acetic acid and boil under a reflux condenser for 2 hours. Add drop by drop to the boiling solution, a solution of 15 grams of anhydrous chromic acid dissolved in 10 cc. of glacial acetic acid and 10 cc. of water. Boil under reflux condenser for two hours, allow to cool and add 400 cc. of cold water, and filter off the precipitated anthraquinone. The

crystals of anthraquinone are washed with hot water, then a hot 1 per cent solution of NaOH, and then with hot water. The residue is dried and weighed and the percentage of anthracene calculated. From 0.25 to 0.75 per cent of anthracene is found in coal tars, and correspondingly larger amounts in coal tar pitches.

A qualitative test to identify the crystals consists in boiling them with zinc dust and caustic soda solution, whereupon an intense red colored solution (Alizarin) is obtained, which decolorizes in contact with the air.

This test will serve to identify coal tar materials in asphalt compositions.

(4) Diazo Reaction—devised by E. Graefe—"Distinction between Lignite Pitches and Other Pitches," Chem. Zeit. *30*—298—(1906), serves to distinguish those bituminous substances containing phenolic bodies from those not containing them, as asphalts. It should be made on the original bituminous substance. In the absence of coal tar materials, this test will establish the presence of wood tars and pitches in asphaltic mixtures especially with a positive Liebermann Storch reaction.

(F) *Physical Tests:*

While the foregoing tests will give some information about the composition and quality of these materials, and their suitability for the purpose intended, the following physical tests are at times more valuable for determining the adaptability of a material for a particular use.

(1) Time of drying or setting on prepared roofing, metal, concrete, etc.

(2) Heat test at 140°F.

(3) Exposure test outdoors at angle of 45° to the south for periods varying from one week to a month.

(4) Baking test.

(5) Toughness.

(6) Working Properties.

(7) Resistance to water, lubricating oil, and acids.

(8) Heat test on smoke stack paint at 410°F.

(9) Adhesion tests.

CHAPTER XXV.

ANALYSIS OF WHITE PAINT PIGMENTS

The vehicle having been extracted from the paint under examination, by the previously outlined methods, see pages 90 to 94, the pigment is left ready for analysis. The pigment can be readily classified under one of the following heads by its color, thus shortening any preliminary examination. Many of the colors have a white base which necessitates a determination of both the colored portion of the pigment and of any white base which may have been used.

The general analysis of colored pigments is carried out according to the specific method outlined for the individual colored pigments, together with the methods for a composite white paint, provided a qualitative examination does not directly reveal the identity of the pigment.

The pigments used in the manufacture of paints are classified as follows, in certain instances the trade names being given by which the particular pigments are shown.

WHITE PIGMENTS

Lead Pigments

Corroded White Lead—Basic Carbonate of Lead.
Old Dutch Process White Lead.
Quick Process White Lead.
Mild Process White Lead.
Carter Lead.

Sublimed White Lead—Basic Sulphate of Lead—Basic Sulphate-White Lead.

Zinc Lead.

Leaded Zinc.

Zinc Pigments

Zinc Oxide—Zinc White.

Lithopone — Alabalith — Ponolith — Beckton White—Charlton White—Orr's White.

Other Opaque White Pigments

Titanium Oxide—Titanox.
Antimony Oxide.

Silica Pigments

Silica—Silex.
Asbestine—Talcose.
China Clay—Kaolin—Tolamite.

Calcium Pigments

Whiting—Paris White—Chalk—Alba Whiting—Spanish White.
Gypsum—Plaster of Paris—Terra Alba—Agalite.

Barium Pigments

Barytes—Barite—Blanc Fixe—Barium Sulphate.
Barium Carbonate—Witherite.

RED AND BROWN PIGMENTS

Red Lead—Orange Mineral.
Vermilions—Para Reds.
Ochres—Tuscan Red—Indian Red—Venetian Red.
Umbers—Siennas.

BLUE PIGMENTS

Sublimed Blue Lead.
Ultramarine Blue.
American Blue—Prussian Blue—Antwerp Blue—Chinese Blue.

YELLOW AND ORANGE PIGMENTS

Chrome Yellow—Lemon Yellow—Medium Chrome Yellow.
American Vermillion—Orange Chrome—Basic Lead Chromate.
Orange Mineral.

GREEN PIGMENTS

Chrome Green.
Chromium Oxide.
Green Earth.

BLACK PIGMENTS

Graphite.
Carbon Black—Bone Black—Lamp Black—Drop Black—Ivory Black—Mineral Black.
Willow Charcoal.
Black Oxide of Iron.

CORRODED WHITE LEAD

BASIC CARBONATE OF LEAD—OLD DUTCH PROCESS WHITE LEAD—QUICK PROCESS WHITE LEAD—MILD PROCESS WHITE LEAD

Corroded white lead contains approximately 80 per cent metallic lead and 20 per cent carbonic acid and combined water with traces sometimes of silver, antimony and other metals. This material should approach the composition indicated by the formula $2PbCO_3.Pb\ (OH)_2$.

Total Lead (*Gravimetric*).—Dissolve 1 gram in 20 cc. of HNO_3 (1: 1) in a covered beaker, heating till all CO_2 is expelled; wash off cover, add 20 cc. of H_2SO_4 (1: 1) and evaporate to fumes of SO_3, cool, add about 150 cc. of water and 150 cc. of ethyl alcohol; let stand in cold water one hour, filter on a Gooch crucible, wash with 95 per cent ethyl alcohol, dry at 110° C., and weigh the $PbSO_4$. Calculate to PbO or to basic carbonate.* Instead of determining the lead as sulphate, the sample may be dissolved by boiling with acetic acid; then dilute to about 200 cc. with water, make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 cc. of a 10 per cent solution of potassium dichromate; heat till the yellow precipitate assumes an orange color. Let settle and filter on a Gooch crucible, washing by decantation with hot water till the washings are colorless, finally transferring all of the precipitate. Then wash with 95 per cent ethyl alcohol and then ether; dry at 110° C. and weigh $PbCrO_4$. (Any insoluble matter should be filtered out before precipitating the lead.) Factor .6375 gives lead content.

Total Lead (*Volumetric*).—Dissolve 0.5 gram of sample in 20 cc. of (1:1) hydrochloric acid and 2 grams sodium chloride, boil till solution is effected, cool, dilute to 40 cc. and neutralize with ammonium hydroxide. Add acetic acid until distinctly acid, dilute to 200 cc. with hot water, boil and titrate with ammonium molybdate as follows:

Dissolve 4.25 grams of ammonium molybdate in water and make up to one liter. To standardize this solution, dissolve about 0.2 gram of pure lead foil in nitric acid (pure PbO or $PbSO_4$ may also be used), evaporate nearly to dryness, add 30 cc. of water, then 5 cc. H_2SO_4 (sp. gr. 1.84), cool, and filter.

Drop filter with $PbSO_4$ into a flask, add 10 cc. concentrated HCl, boil till completely disintegrated, add 15 cc. of HCl, and 25

* This method of weighing lead sulphate is not accurate in the presence of calcium compounds.

cc. of ammonium acetate slightly acidified with acetic acid. Acidify with acetic acid, dilute to 200 cc. with hot water and boil. Titrate, using an outside indicator of one part of tannic acid in 300 parts of water.

It should be noted that when calcium is present, it forms a more or less insoluble molybdate, and results are apt to be high. With samples containing less than 10 per cent of lead, the lead should be precipitated as $PbSO_4$, filtered, redissolved and titrated as in the process of standardizing.

Carbon Dioxide.—Determine by evolution with dilute hydrochloric acid absorbing in soda-lime or KOH solution. Calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

*Acetic Acid.**—Place 18 grams of the pigment in a 500 cc. flask, add 40 cc. of syrupy phosphoric acid, 18 grams of zinc dust and 50 cc. of water. Connect to a straight Liebig condenser, apply heat and distill down to a small bulk. Then pass steam into the flask until it becomes about half full of condensed water, shut off the steam and distill down to a small bulk—this operation being conducted twice. To the total distillate which was collected in a larger flask add 1 cc. of syrupy phosphoric acid, connect to a Liebig condenser, using a spray trap, and distill to a small volume—about 20 cc. Pass steam through till about 200 cc. of water condenses in the distillation flask, shut off steam and continue the distillation. These operations of direct and steam distillations are conducted until 10 cc. of the distillate require only 1 drop of N/10 alkali to give a change in the presence of phenolphthalein. Then titrate the total distillate with N/10 sodium hydroxide and phenolphthalein and calculate the total acidity as acetic acid. It will be found convenient to titrate each 200 cc. portion of the distillate as collected.

*Metallic Lead.**—Weigh 50 grams of the sample into a 400 cc. beaker, add a little water and add slowly 60 cc. of 40 per cent acetic acid and after effervescence has ceased, boil on hot plate. Fill the beaker with water, let settle, and decant the clear solution. To the residue add 100 cc. of a mixture of 360 cc. of strong NH_4OH, 1080 cc. of water, 2160 cc. of 80 per cent acetic acid, and boil until all solution is complete. Fill the beaker with water, let settle and decant the clear solution. Collect residue on a watch-glass, floating off everything but metallic lead. Dry and weigh. Result $\times 2 =$ percentage of metallic lead in sample.

* Thompson's Method, Jour. Soc. Chem. Ind., 24, 487, 1905.

The following method of A. N. Finn (unpublished) gives total basicity of a pure white lead: Place 2 grams of pigment in an evolution flask, add a little CO_2-free water, connect with a separatory funnel and condenser (Knoor type), add through the funnel, finally washing down, 100 cc. of N/4 nitric acid, boil and absorb the CO_2 in a soda lime tube in the usual manner (having H_2SO_4 and $CaCl_2$ drying tubes in train) and weigh. To the solution in the evolution flask, add about 20 cc. of neutral sodium sulphate solution and titrate with N/4 sodium hydroxide solution (carbonate-free), using phenolphthalein. CO_2 is calculated to $PbCO_3$. The amount of N/4 acid corresponding to the CO_2 is calculated and deducted from the total amount of N/4 acid neutralized by the sample and the difference calculated to combined H_2O, from which $Pb(OH)_2$ is computed.

Electrolytic Deposition of Lead.—In samples of pigment which contain less than 5 per cent of lead, the lead content may be determined electrolytically in a very rapid manner by following the procedure as outlined by Smith* in his Electro-Analysis, as follows:

"Twenty cc. of concentrated nitric acid were added to a solution of lead nitrate, giving a total volume of about 125 cc. and acted upon with a current of $N.D._{100} = 10$ amperes and 4.5 volts. The rotating electrode (cathode) performed 600 revolutions per minute. The deposits had a uniform, velvety black color. There was no tendency on the part of the deposit to scale off, though more than a gram of the dioxide was precipitated. The time varied from ten to fifteen minutes. A platinum dish with sand blasted inner surface was used as an anode.

"By using a current of $N.D._{100} = 11$ amperes and 4 volts upon a solution of lead nitrate containing 0.4996 gram of lead or 0.5787 gram of dioxide, the rate of precipitation was found to be:

In 5 minutes........0.4940 gram lead dioxide
In 10 minutes........0.5708 gram lead dioxide
In 15 minutes........0.5747 gram lead dioxide
In 20 minutes........0.5770 gram lead dioxide
In 25 minutes........0.5787 gram lead dioxide
In 30 minutes........0.5789 gram lead dioxide

"The maximum time period for a quarter of a gram of metal metal is twenty-five minutes." See also Interdepartmental Specifications in back of volume.

* Electro-Analysis, Smith: P. Blakiston's Sons & Co.

BASIC SULPHATE OF LEAD

(*Sublimed White Lead*)*

An average approximate analysis of sublimed white lead as commercially placed upon the market should show about 78.5 per cent of lead sulphate, 16 per cent of lead oxide and 5.5 per cent of zinc oxide.

ANALYSIS

Total Sulphates

Mix 0.5 gram of the sample with 3 grams of sodium carbonate in a beaker. Treat the mixture with 30 cc. of water and boil gently for ten minutes. Allow to stand for four hours. Dilute the contents of the beaker with hot water, filter off the residue and wash until the filtrate is about 200 cc. in volume. Reject the residue. By this reaction all the lead sulphate is changed to carbonate, the sulphate being transposed into sodium sulphate, which is found in the filtrate.

Acidulate the filtrate with hydrochloric acid and add an excess of about 2 cc. of the acid. Boil, and add a slight excess of barium chloride solution (12 cc. of an 8 per cent solution). When the precipitate has well settled, 4 hours or preferably over night, filter on an ashless filter, wash, ignite and weigh as $BaSO_4$. Calculate the $BaSO_4$ to $PbSO_4$ by using the factor 2.6, when a half gram sample is used.

Weight of $BaSO_4 \times 1.3$ equals weight $PbSO_4$.

On 0.5 gram sample factor $BaSO_4$ to $PbSO_4 = 2.6$.

TOTAL LEAD

Molybdate Method.†—Dissolve 1 gram of the sample in 100 cc. of an acid ammonium acetate solution made up as follows:

Eighty per cent acetic acid.............	125 cc.
Concentrated ammonium hydroxide......	95 cc.
Water	100 cc.

Add this solution hot and dilute with about 50 cc. of water. Boil until dissolved.

Dilute to 200 cc. and titrate with standard ammonium molybdate solution, spotting out on a freshly prepared solution of tannic acid.

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* Schaeffer Method.

† Modification of Low's Method. Technical Methods of Ore Analysis, Low, p. 149.

Ammonium molybdate is a slightly variable salt, but a solution containing 8.67 grams per liter usually gives a standard solution:

1 cc. equals 0.01 gram Pb.

Standardize against pure PbO or pure $PbSO_4$.

Bichromate Method.—Treat the sample as above described until dissolved. If the solution is not quite clear, filter. Add to the filtrate an excess of neutral potassium bichromate solution. Boil until the lead chromate has become an orange yellow color and stand in a warm place until the precipitate has settled. Filter on a Gooch crucible, wash thoroughly, ignite below a red heat and weigh as $PbCrO_4$.

The $PbCrO_4$ may be estimated volumetrically by titrating the chromic acid present. For this method, dissolve the lead chromate from off the filter with hydrochloric acid. Wash well and determine the chromic acid present with a standard solution of ferrous ammonium sulphate, using a dilute solution of potassium ferricyanide as an outside indicator. The ferrous ammonium sulphate is made up of such strength that 1 cc. will equal 0.00202 gram Fe. For a one gram sample divide the number of cc. of ferrous ammonium sulphate used by 4.

Deduct the lead found as lead sulphate from the total lead and calculate the residual lead to PbO.

TOTAL ZINC*

Boil one gram of the sample in a beaker with the following solution:

Water	30 cc.
Ammonium chloride................	4 grams
Concentrated hydrochloric acid......	6 cc.

If the sample is not quite dissolved the result is not affected, as the residue is lead sulphate or precipitated lead chloride.

Dilute to 200 cc. with hot water, add 2 cc. of a sautrated sodium thiosulphate solution and titrate with a standard solution of potassium ferrocyanide, spotting out on a 5 per cent solution of uranium nitrate. Calculate the zinc to zinc oxide by multiplying by the factor 1.245.

TOTAL IRON OXIDE

Determine this constituent as outlined under the Analysis of Litharge.

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* Low's Technical Methods of Ore Analysis.

THE LEAD CONTENTS IN SUBLIMED WHITE LEAD—A CALCULATION*

The composition of sublimed white lead, the basic sulphate of lead, has become a most important factor to users of this pigment. Both among rubber manufacturers and producers of paints, it is being found essential that the contents of lead oxide and lead sulphate be known, so that advantage may be fully taken of its characteristic properties. This control necessitates an analysis of the compound in the laboratory.

In analyzing sublimed white lead by the usual method, it is found that the percentage composition can be determined only by an analysis entailing lengthy manipulation, in which the content of lead oxide is directly dependent upon the accuracy of the other determinations, owing to the necessity of estimating its percentage by a calculation based upon the percentage of the other constituents present. The steps in the procedure must therefore be closely watched for slight inaccuracies at all times.

As is well known, the average composition of sublimed white lead is given as follows:

Lead sulphate	78.5
Lead oxide	16.0
Zinc oxide	5.5

That its composition varies only slightly from the above analysis during a long period of time, is shown by its comparison with an average of the entire output of the Eagle-Picher Lead Company extending over five months' time an average embracing 270 total analyses.

This average shows the composition to be:

Lead sulphate	76.68
Lead oxide	17.23
Zinc oxide	5.79
	99.70

A slightly higher lead oxide and zinc oxide content and a correspondingly lower lead sulphate content is found, than in the usually stated formula. It shows, however, only slight variation. The average total percentage, consisting of lead sulphate, lead oxide, and zinc oxide, was found to be 99.70 per cent. The remaining 0.3 of a per cent is only rarely determined, and when actually sought is found to consist of moisture, occluded gas

* J. Ind. & Eng. Chem., 6, 200 (1914).

and ash. A definite ratio exists between the total lead content and the lead sulphate and lead oxide contents, and advantage may be taken of this relation for a rapid and accurate determination of the lead constituents in sublimed white lead.

In order to arrive at the short method for the analysis which is based upon a direct calculation of the lead and zinc contents, it is necessary that only the percentage of zinc and lead be determined by the methods already described.

Using the percentages of zinc oxide and total lead, together with the average total, 99.70 per cent, determined from the large number of analyses, the contents of lead oxide and lead sulphate are readily estimated by the following calculation:

Total percentage of lead compounds present equals 99.70 per cent (average) = total percentage found of ZnO, PbO and $PbSO_4$ less percentage ZnO.

Total percentage of lead compounds present equals 99.70 per cent (average total) minus percentage ZnO.

Atomic weight lead	207.1
Molecular weight lead oxide	223.1
Molecular weight lead sulphate	303.1

As a hypothetical case, we can assume the presence of a 4.70 per cent ZnO and 69.00 per cent metallic lead.

$$(1)\quad \frac{\left(\dfrac{\text{Mol. wt. } PbSO_4}{\text{At. wt. Pb.}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\dfrac{\text{Mol. wt. } PbSO_4 - \text{mol. wt. } PbO}{\text{Mol. wt. } PbO}} = \%\ PbO \text{ present}$$

$$(2)\quad \frac{\left(\dfrac{\text{Mol. wt. } PbO}{\text{At. wt. Pb}} \times \%\ \text{Pb found}\right) - \%\ \text{Pb constituents}}{\dfrac{\text{Mol. wt. } PbO - \text{Mol. wt. } PbSO_4}{\text{Mol. wt. } PbSO_4}} = \%\ PbSO_4 \text{ present}$$

Determining the percentage of lead oxide and lead sulphate present by the above formulas we find:

$$(1)\quad \frac{\left(\dfrac{303.1}{207.1} \times 69.00\right) - 95.00}{\dfrac{303.1 - 223.1}{223.1}} = \text{per cent } PbO = 16.68$$

$$(2)\quad \frac{\left(\dfrac{223.1}{207.1} \times 69.00\right) - 95.00}{\dfrac{223.1 - 303.1}{303.1}} = \text{per cent } PbSO_4 = 78.32$$

Therefore by substituting the percentages of lead and zinc oxide in the following formula which is derived from equation (1) the percentage of PbO in the sublimed white lead is easily found. The sum of the percentages of zinc oxide and lead oxide subtracted from 99.7 gives the percentage of lead sulphate.

$$\text{Per cent PbO} = [1.464 \times \%\ \text{Pb} - (99.7 - \%\ \text{ZnO})]\ 2.79.$$

A comparison of the actual results obtained by the complete analysis of sublimed white lead and its calculated composition shows that the values obtained are concordant. Indeed the only essential factors for the short method are accurate determinations of the lead and zinc contents. The removal of several steps in the analysis leads to greater accuracy coupled with a considerable curtailment of time.

A table of comparisons shows the following concordance of results:

TABLE XXIX

No.	Analysis	Lead sulphate	Lead oxide	Zinc oxide	Total lead	Total
1	Complete	79.20	15.28	5.23	68.30	99.72
	Calculated	79.17	15.30	....	.....	.....
2	Complete	77.74	16.81	5.11	68.70	99.66
	Calculated	77.97	16.62	....	.....	.....
3	Complete	77.09	16.95	5.73	68.40	99.77
	Calculated	76.85	17.12	....	.....	.....
4	Complete	80.20	14.66	4.86	68.40	99.72
	Calculated	80.15	14.69	....	.....	.....
5	Complete	78.00	16.60	5.11	68.70	99.71
	Calculated	77.97	16.62	....	.....	.....
6	Complete	77.84	17.10	4.86	69.00	99.80
	Calculated	77.69	17.15	....	.....	.....
7	Complete	77.22	16.20	6.23	67.80	99.63
	Calculated	77.41	16.06	....	.....	.....
8	Complete	74.10	20.21	5.48	69.40	99.79
	Calculated	74.00	20.22	....	.....	.....
9	Complete	77.63	15.92	6.23	67.80	99.78
	Calculated	77.41	16.06	....	.....	.....
10	Complete	76.05	17.93	5.73	68.60	99.71
	Calculated	76.04	17.93	....	.....	.....
11	Complete	76.98	17.78	4.98	69.10	99.74
	Calculated	76.85	17.87	....	.....	.....

That this method will prove of value will be readily appreciated by all chemists who have to determine the percentage composition of any basic sulphate of lead, either for the purpose of meeting specifications or for accurate control of finished products.

Graphic Analysis of Sublimed White Lead.—In order to escape the determination of SO_3 and at the same time eliminate the calculations the accompanying chart was devised by Burton Paxton.* The left hand scale of the chart is graduated from 5 to 10, representing percentage of zinc oxide in the pigment. Right-hand scale is graduated from 65 to 70, representing total lead in the pigment. The two center scales are graduated in terms of lead sulphate and lead oxide. A line drawn across the chart connecting any point (*a*) on the ZnO scale with any point (*b*) on the Pb scale will intersect the center scales at percentages of lead sulphate and lead oxide contained in pigment having *a* per cent of ZnO and *b* per cent of Pb.

To use the chart it is necessary to have percentages of Pb and ZnO in the pigment. These may be determined quite rapidly by volumetric methods as follows:

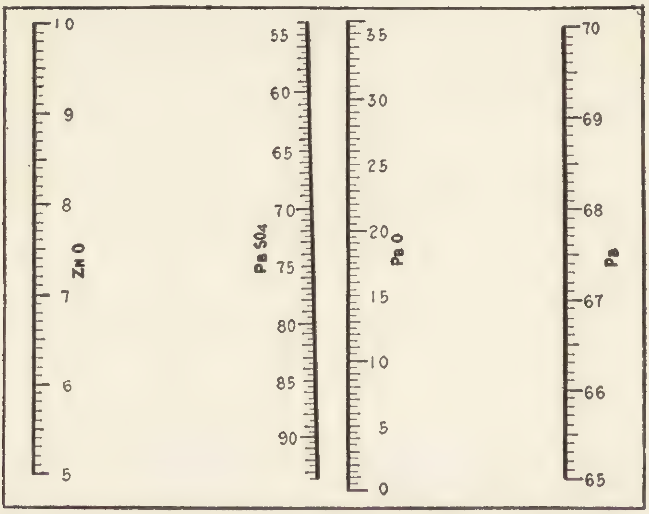

FIG. 51—Chart for Graphic Analysis of Sublimed White Lead

For ZnO.—Boil 1 gram of pigment in 6 cc. HCl, 30 cc. H_2O and 5 grams NH_4Cl. Pigment will not all dissolve, but this has no effect on result. Dilute to 250 cc. with hot water, add a few drops of 10 per cent sodium sulphite solution and titrate with a standard solution of potassium ferrocyanide, using ammonium molybdate as an outside indicator. Ferrocyanide solution should equal 0.01 gram ZnO per cc.

* Above method and chart as published by Burton Paxton in Chem. & Met. Eng., May 24, 1922.

For Lead.—Dissolve 1 gram of pigment in acid ammonium acetate and dilute to 200 cc. Heat to boiling and titrate hot with a standard solution of ammonium molybdate, using tanic acid as an outside indicator. Molybdate solution should equal 0.01 gram of Pb per cc.

Now lay straightedge across chart connecting percentage of ZnO on left-hand scale with percentage of Pb on right-hand scale. Intersection of this line with center scales will give percentages of $PbSO_4$ and PbO. The sum of percentages of ZnO, $PbSO_4$ and PbO is, for all practical purposes, a constant, 99.7 per cent.

Using this chart, it is possible to make an analysis of pigment in 10 or 15 minutes.

See also Interdepartmental Specifications in back of volume.

LEADED ZINC

Leaded zinc is a varying compound containing zinc oxide and lead sulphate, the latter running from 5 to 35 per cent.

Moisture.—Heat 2 grams at 105° C. for two hours.

Lead and Zinc.—Determine the lead directly by the volumetric molybdate method and the zinc by the volumetric ferrocyanide method as outlined under Basic Sulphate-White Lead.

*Total Soluble Sulphates.** (In the absence of $BaSO_4$).—Treat 0.5 gram of the sample with 5 cc. of water, 3 grams of NH_4Cl and 5 cc. of HCl saturated with bromine; digest (covered) on the steam bath about fifteen minutes, add 25 cc. of H_2O, neutralize with dry Na_2CO_3 and add about 2 grams more. Boil ten to fifteen minutes; let settle, dilute with hot water, filter and wash with hot water; redissolve in HCl, reprecipitated as above and wash thoroughly with hot water. Acidify the united filtrates with HCl and add a slight excess of 10 per cent $BaCl_2$ solution. Let stand on steam bath for one hour, filter, wash with hot water, ignite and weigh the $BaSO_4$. Calculate to SO_3 (includes SO_3 formed from SO_2).

Total Soluble Sulphate (in the presence of $BaSO_4$).—Treat 1 gram in a 600 cc. beaker with 10 cc. of H_2O, 10 cc. of strong HCl, saturated with bromine, and 5 grams of NH_4Cl, heat on a steam bath in a covered beaker for five minutes, add hot water to make about 400 cc., boil for five minutes and filter to separate

* Report of Sub-committee VIII of Committee D-1, Proceedings of American Society for Testing Materials, 14, 271-2, 1914.

any insoluble material. (A pure pigment should be completely dissolved.) Wash with hot water, ignite and weigh the insoluble. Remove lead with Na_2CO_3 as above, making a double precipitation, acidify, and to the boiling hot filtrate add slowly, with stirring, 20 cc. of a 10 per cent $BaCl_2$ solution; let stand for two hours on the steam bath, filter, wash, ignite, and weigh as $BaSO_4$. (Includes SO_3 formed from SO_2.)

Soluble Zinc Sulphate.—Boil 2 grams of the sample with 150 cc. of water and 50 cc. of alcohol for thirty minutes, filter and wash with a mixture of alcohol and water (1:3). Heat the filtrate to boiling and expel most of the alcohol; then determine SO_3 by the usual method of precipitation with $BaCl_2$. Calculate to $ZnSO_4$ and to SO_3.

Sulphur Dioxide.—Digest 2 grams of the sample with frequent stirring in 100 cc. of freshly boiled cold water and 5 cc. of concentrated HCl; let stand ten to fifteen minutes, add an excess of 0.01 normal iodine solution and titrate back with 0.01 normal sodium thiosulphate solution, using starch indicator. Report as SO_2. Run blank on reagents and make corrections.

Calculations.—Report soluble SO_3 as $ZnSO_4$. Deduct ZnO equivalent of the $ZnSO_4$ from total ZnO and report residue as ZnO. Deduct soluble SO_3 and SO_3 equivalent to SO_2 from total SO_3, calculate remainder to $PbSO_4$; subtract PbO equivalent of $PbSO_4$ from total PbO and report remainder as PbO. See also Interdepartmental Specifications in back of volume.

ANALYSIS OF ZINC OXIDE

Total Zinc.—Dissolve 0.25 to 0.3 g. in 10 cc. of concentrated HCl and 20 cc. of H_2O, make alkaline with NH_4OH, then acid with HCl, add 3 cc. more of concentrated HCl, dilute to about 250 cc. with H_2O, heat nearly to boiling and titrate with standard potassium-ferrocyanide solution. Report as ZnO (Includes Cd). Iron, copper or other interfering substances should be first removed.

Total Soluble Sulphur.—Moisten a 10 g. sample with water, add a few drops of bromine and then concentrated HCl, boil to expel bromine. A small strip of aluminum is added and the solution heated gently to throw out any lead that may be present. Now filter off the lead and insoluble and wash with hot water. Make alkaline with NH_4OH, then just slightly acid with HCl, heat to boiling and add about 15 cc. of hot barium-chloride solution. Let stand several hours (overnight), filter on a

weighed Gooch crucible, wash well with hot water, dry, ignite for five minutes, cool and weigh as $BaSO_4$. Calculate to S.

Sulfur Dioxide.—Mix 5 g. of sample with 50 cc. of warm (freshly boiled and then partly cooled) water to an emulsion and pour into a glass-stoppered flask containing 18 cc. of HCl and exactly 25 cc. of N/10 iodine solution, stopper and shake until all the oxide is dissolved. Titrate the excess of iodine as rapidly as possible with N/10 sodium-thiosulfate solution. Use starch indicator. Calculate to SO_2.

Soluble Zinc Sulfate.—Determine as under Leaded-Zinc.

Lead Oxide Determination by the Breyer-Croll Electrolytic Method.—9.330 grams of the sample are dissolved in a 250 cc. beaker with 40cc. of concentrated HNO_3 and about 100 cc. of distilled water. The solution is boiled for a few minutes until all red fumes are expelled. Add enough silver nitrate to precipitate all chlorides. Electrolyse for two hours, using about 0.5 ampere and a solid sheet platinum anode. The solutions are tested for lead before turning off the current by raising the liquid in the beaker and allowing to continue for twenty minutes. If there is no fresh deposit of PbO_2, the electrode is washed three times with distilled water (current still on).

After drying one hour at 110° C., the electrode is weighed. The weight of PbO_2 in milligrams divided by 100 gives the percentage of PbO.

The above method is satisfactory for routine work on zinc oxide. Where a detailed analysis of other impurities is important, the following method may be used.

Ferric Oxide.—Treat 10 grams with 50 cc. strong HCl, add about 1 gram $KClO_3$, and boil down to a syrupy consistency. Cool, add water and a large excess of ammonia. Allow to stand until the ferric oxide separates, and filter; wash with dilute ammonia water and then with hot water. Dissolve the precipitate of ferric oxide in an Erlenmeyer flask with warm dilute H_2SO_4. Wash the filter paper thoroughly with hot water, dilute the solution in the Erlenmeyer flask to about 200 cc. and pass in hydrogen sulphide for five minutes. Place a funnel in the neck of the flask and boil until all H_2S is expelled. Cool and titrate with dilute $KMnO_4$. A blank determination is carried out in a similar manner and the number of cc. of $KMnO_4$ required to give a pink color is subtracted from the total number required on the sample.

Manganese Oxide.—Treat a 10 gram sample in a 16 ounce Erlenmeyer flask with 100 cc. of HNO_3 (1:3), heat to boiling and add a pinch of sodium bismuthate, when the pink color of permanganic acid is produced; now add a few cc. of dilute $Na_2S_2O_3$ solution to destroy the pink color, and continue boiling to drive off all nitrous oxide fumes. Cool thoroughly and add 50 cc. of a 3 per cent solution of HNO_3, and a very small pinch of sodium bismuthate to restore the pink color again. Filter the solution through a Gooch crucible to remove the excess of sodium bismuthate, rinsing the flask and Gooch with 50 cc. of 3 per cent HNO_3 solution to which a small amount of sodium bismuthate has been added. Now add 10 cc. of ammonium ferrous sulphate solution, and titrate the excess of ammonium ferrous sulphate with standard $KMnO_4$ whose iron value has been determined. One gram of $KMnO_4$ per liter is a convenient strength; and 12.4 grams of ammonium ferrous sulphate, and 50 cc. strong H_2SO_4 to the liter gives a solution which is almost equal to the permanganate solution. A blank determination is carried out in exactly the same manner as with the sample of oxide, and the difference in the number of cc. of $KMnO_4$ required to give a pink color with the blank determination and the sample of oxide is equal to the amount of MnO present. The manganese value of the $KMnO_4$ is calculated from the iron value, according to the ratio of Mn : Fe, or 55 : 279.5 or 0.1968 : 1.

Arsenious Oxide.—Weigh 10 grams of oxide in a 16-ounce Erlenmeyer flask, add about 10 grams of $FeSO_4$, place a rubber stopper with an acid delivery tube and an exit tube, which is immersed in a beaker containing about 200 cc. distilled water. The beaker of water is placed in a pan of cold water, the pan having an inlet and overflow. Now add 100 cc. strong HCl from the delivery tube, and heat the flask to boiling so as to distill the arsenic into the beaker of water. Continue boiling until about two-thirds of the acid has been distilled, remove from the flame, rinse the delivery tube, add 10 cc. strong HCl to the solution in the beaker, warm and pass in H_2S to precipitate the arsenic, as As_2S_3. Let stand in a warm place for some time and filter in a Gooch crucible, wash the precipitate of As_2S_3 with alcohol and then with carbon bisulphide and several times with dilute alcohol. Dry at 105° C. for one hour and weigh. Dissolve the As_2S_3, in the Gooch crucible with dilute ammonia water, wash well with hot water, and dry at 105° C. and reweigh. The loss in weight is As_2S_3, from which the As_2O_3 may be calcu-

lated. See procedure for arsenic, p. 34 in Standard Methods of Chemical Analysis, Scott (D. Van Nostrand Co.) Cuprous chloride used in this method.

Chlorine.—Ten grams of the sample are covered with water and 10 cc. of N/10 $AgNO_3$ solution, which has been standardized against pure NaCl, added. Forty cc. of concentrated HNO_3 are added and the solution boiled until nitrous fumes are removed. It is then cooled, 5 cc. of ferric nitrate solution (1:6) added and the solution titrated to a faint pink with N/10 ammonium sulfocyanide (NH_4CNS). A blank shall be run with the same reagents, to determine the relative strengths of the solutions.

Acid Insoluble.—A sample of 10 grams is treated with 25 cc. of water and 25 cc. of hydrochloric acid and evaporated to dryness. The residue is taken up with 50 cc. of 1:4 hydrochloric acid and the insoluble filtered off and *thoroughly* washed with 1:4 hydrochloric acid and then with boiling water. It is further washed with hot ammonium acetate solution and again with boiling water. The insoluble is then burned off and weighed.

Water Soluble Salts.—Five grams of the sample are shaken in a 500 cc. graduated flask for 10 minutes with 250 cc. of water at room temperature. The solution is made up to exactly 500 cc. and filtered through dry paper. One hundred cc. of the clear filtrate are measured out, poured into a weighed platinum dish and evaporated to dryness on a sand-bath, the contests being protected from dust. The residue is dried for one or two hours at 110° C., cooled and weighed rapidly. The increase in weight represents the water soluble salts.

ANALYSIS OF LITHOPONE

ALBALITH, PONOLITH, BECKTON WHITE, STERLING WHITE, SUNOLITH, ETC.

This pigment is a chemically precipitated pigment containing approximately from 69 to 70 per cent barium sulphate, the remainder consisting of zinc sulphide, with occasional impurities of zinc oxide and carbonate.

Moisture.—Heat 2 grams for two hours at 105° C.

Water Soluble.—Determine as under zinc oxide.

Insoluble and Total Zinc.—Take 1 g. of the sample in a 200 cc. beaker, add 10 cc. of concentrated HCl, mix, and add in small portions about 1 g. of $KClO_3$, then heat on the steam

bath until about half of the liquid is evaporated. Dilute with H_2O, add 5 cc. of dilute H_2SO_4 (1:10); boil, let settle, filter, wash, ignite, cool, and weigh the insoluble which should be only $BaSO_4$; make a qualitative examination for alumina and silica. The insoluble should be examined under the microscope for the presence of natural crystallin barytes. Sample may also be examined direct. Make filtrate from insoluble alkaline with NH_4OH, acid with HCl, add 3 cc. of concentrated HCl, dilute to about 250 cc. with H_2O, heat nearly to boiling and titrate with $K_4Fe(CN)_6$ solution as under zinc white. Calculate to Zn.

Zinc Oxide.—Treat a 4 g. sample of the lithopone for 4 hours with 200 cc. of 1 per cent acetic acid at room temperature, stirring occasionally. Filter by suction on a double filter paper and wash with cold water; add to the clear filtrate 13 cc. of concentrated NH_4OH, neutralize with HCl and then add 3 cc. of concentrated HCl in excess. Heat to boiling and titrate with $K_4Fe(CN)_6$, using uranium-acetate solution as an outside indicator. Calculate to ZnO. Calculate this result to Zn, subtract from total Zn, and calculate the difference to ZnS. (Any $ZnCO_3$ or $ZnSO_4$ is included in the ZnO.)

*Zinc Sulfide.**—Place 0.5 g. of pigment in evolution flask with about 10 g. of "feathered" or mossy zinc, add 50 cc. of water; insert the stopper carrying a separatory funnel and an exit tube. Run in 50 cc. of concentrated HCl from the funnel, having previously connected the exit tube to two absorption flasks in series; first flask contains 100 cc. of alkaline lead-nitrate solution; second flask, 50 cc. of same as a safety device. After all of the acid has run into the evolution flask, heat slowly, finally boiling until the first appearance of steam in the first absorption flask; disconnect, let the lead sulfide settle, filter, wash with cold water, then with hot water till neutral to litmus paper and washings give no test for lead. The PbS precipitate is dissolved in hot, dilute HNO_3, evaporated to fumes with H_2SO_4 and finally weighed as $PbSO_4$. Calculate PbS or $PbSO_4$ to ZnS.

The alkaline lead solution is made as follows: Into 100 cc. of KOH solution (56 g. in 140 cc. of H_2O) pour a saturated solution of lead nitrate (250 g. in 500 cc. of H_2O) until the precipitate ceases to redissolve, stirring constantly while mixing. About 3 volumes of the lead solution will be required for one of the alkali.

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* Evolution Method of W. G. Scott, "White Paints and Painting Materials," p. 257; see also Blair, "Chemical Analysis of Iron."

Instead of absorbing the evolved H_2S in alkaline lead-nitrate solution, a solution of 8 g. of cadmium chloride in 250 cc. of water and 150 cc. of NH_4OH (sp. gr. 0.90) may be used. The CdS precipitate may be filtered on a weighed Gooch, washed with water containing a little NH_4OH, dried at 100° C., and weighed. Calculate to ZnS. It is better to filter the CdS on a small filter and wash as above, then place filter and precipitate in a beaker and dissolve in HCl and $KClO_3$ (keeping at room temperature at first), filter out any paper pulp or insoluble matter; make filtrate alkaline with NH_4OH, then just acid with HCl, heat to boiling and precipate with $BaCl_2$ in usual manner. Filter, wash, ignite, and weigh $BaSO_4$. Calculate to ZnS.

For very rapid work the contents of the absorption flask after all H_2S has been absorbed, may be washed into a vessel with *cold* water and diluted to about one liter, acidified with concentrated HCl and titrated with standard iodine solution, using starch indicator. (The precipitate should be completely dissolved.) The iodine solution is prepared by dissolving about 12.7 g. of pure resublimed iodine and 18 g. of KI in a little water and then diluting to one liter.

While the above methods have proved generally satisfactory, the evolution method for zinc sulfide is rather tedious. Breyer and Croll of the N. J. Zinc Co. omit this method and secure the zinc sulfide content by difference, after determining total zinc and barium sulfate. Their methods for the latter as communicated recently to the writer, are given below:

Total Zinc in Lithopone (*B*×*C Method*).—A 2 gram sample is weighed out into a 150 cc. beaker and treated with 25 cc. concentrated hydrochloric acid. When action has largely ceased, 50 cc. of 1:1 sulphuric acid is added, evaporated to fumes and the heating continued, with beaker covered, until all barium sulphate has gone into solution. After cooling, cold water is poured in to nearly fill the beaker. The solution and reprecipitated barium sulphate are then poured into a graduated 500 cc. flask, water added to the mark and the whole thoroughly mixed and filtered. A 250 cc. portion of the clear filtrate is measured out into a 600 cc. beaker, 20 cc. of citric acid solution and 10 cc. of ferric nitrate solution added. The excess acid is neutralized with ammonia, using litmus paper, and a definite excess of 15 cc. of ammonia added.

The solution is brought to a boil and then the titrating solution of potassium ferrocyanide is run in with constant stirring

until within 1 cc. of the end point. The addition is continued 0.2 cc. at a time until all the zinc has been precipitated as indicated by a blue coloration appearing when a drop of the solution is added to a few drops of acetic acid on a test plate.

The potassium ferrocyanide solution is standardized by starting with a weighed amount of C.P. zinc approximately equal to the amount to be titrated in the sample, and carrying through the same procedure.

Barium Sulphate in Lithopone (*B* $\times$ *C Method*).—A 1-gram sample is weighed out into a platinum crucible, mixed with 6-8 grams of sodium carbonate and fused for twenty minutes over a Bunsen Burner and twenty minutes over a blast lamp. The fusion is then leached out with about 200 cc. of hot water in a 250-cc. beaker. The insoluble barium carbonate is filtered off and washed thoroughly with hot sodium carbonate solution (2 grams per liter). The barium carbonate is then dissolved from the paper into a 600-cc. beaker with hot 1:4 hydrochloric acid, washing thoroughly. The solution is diluted to about 400 cc. neutralized with ammonia and then made slightly acid with hydrochloric acid (2 cc. excess). The solution is heated to boiling and barium sulphate precipitated with hot ammonium sulphate solution (40 grams per liter). After standing four hours on a steam plate, the barium sulphate is filtered off on to a weighed, ignited Gooch crucible, ignited and weighed. See also Interpartmental Specification in back of volume.

ANALYSIS OF DRY TITANOX

The recent advent of titanium oxide as a constituent of white paints should be of interest to analytical chemists, since special methods are necessary for the determination of the titanium present. There is given below L. E. Barton's method for the analysis of dry titanium oxide pigment such as is made in the United States and which usually contains 75% barium sulphate and 25% titanium oxide. There is also given a method for the separation of zinc and lead from mixtures containing titanium.

Determination of Barium Sulphate.—Weigh ½ gram sample into 250 cc. Pyrex glass beaker; add 20 cc. concentrated sulphuric acid and 7 or 8 grams sodium sulphate. Mix well and heat on hot plate until fumes of sulphuric anhydride are evolved and then heat directly over flame to boiling for five minutes or until solution is complete. Traces of silica, if any, remain as an insoluble residue.

Cool, take up with 100 cc. of water, boil and filter off barium sulphate and silica, washing with 5 per cent sulphuric acid to free residue from titanium.

Determination of Titanium.—The volumetric method used for determination of titanium is essentially that described by P. W. & E. B. Shimer (Proc. Eighth Internat. Congress of Applied Chem.); the method hereafter described differing principally in the form of reductor and also in a few details of operation.

Reagents.—Standard ferric ammonium sulphate solution. Dissolve 30 grams of ferric ammonium sulphate in 300 cc. water acidified with 10 cc. of sulphuric acid; add potassium permanganate drop by drop as long as the pink color disappears, to oxidize any ferrous to ferric iron; finally dilute the solution to one liter.

Standardize this solution in terms of iron. The iron value multiplied by 1.4329 gives the value in titanic oxide (TiO_2); and iron value multiplied by .86046 gives the value of the solution in terms of metallic titanium.

Indicator.—Saturated solution of potassium thiocyanate.

Reductor.—As a reductor a 500 cc. dispensing burette is used. The internal dimensions of the burette are 1⅝ inches by 22 inches.

The reductor is charged with 1200 grams of 20 mesh amalgamated zinc, making a column about 12 inches high and having an interstice volume of about 135 cc. This form of reductor is convenient, and when used as hereafter described is adapted to maintaining hot solutions, which is essential for complete reduction of the titanium.

The reductor is connected to a liter flask for receiving the reduced titanium solution through a three-hole rubber stopper, which carries also an inlet tube for carbon dioxide supply and an outlet tube for connecting with the suction pump.

The reductor is prepared for use by first passing through it a little hot dilute sulphuric acid followed by hot water, finally leaving sufficient hot water in the reductor to fill to the upper level of the zinc.

The hot filtrate from the barium sulphate determination is now introduced; about 10 cc. of water being drawn from the reductor into the original beaker to bring the solution to about the upper level of the zinc. The water thus removed will not contain any titanium if the operation has been conducted as

described, but it serves as a safeguard and is also convenient to acidify this water with 10 cc. sulphuric acid and reserve it on the hot plate to be used as an acid wash after the reduction of the sample solution.

The titanium solution is allowed to remain in the reductor for 10 minutes.

While the solution is being reduced, the receiving flask is connected to the reductor and the air completely displaced by carbon dioxide, conveniently drawn from a cylinder of the liquified gas.

When the reduction is complete the receiving flask is connected with the suction pump, and while still continuing the flow of carbon dioxide the reduced solution is drawn out, followed by the reserved acid wash and then three or four 100 cc. washes with hot water. The displacement of the sample solution and washing of the zinc is so regulated by means of the stopcock that the reductor is always filled with solution or water to the upper level of the zinc.

When the washing is complete, gradually release the suction to prevent air being drawn back into the receiving flask.

Disconnect the flask, add 5 cc. of potassium thiocyanate solution as indicator and titrate immediately with standard ferric ammonium sulphate solution, adding the solution rapidly until a brownish color is produced, which will remain for at least one minute.

ANALYSIS OF PAINTS CONTAINING TiO_2

After the pigment has been extracted and dried, a sample is weighed out and decomposed by the ordinary acid treatment. Weigh 1 gram into a 250 cc. Pyrex beaker; add 40 cc. concentrated sulphuric acid and 15 grams sodium sulphate. Mix well and heat on a hot plate until fumes of SO_3 are evolved, and then continue heat to boiling for five minutes. Silica, if present, will, of course, remain undissolved. Cool, take up with 200 cc. water, boil and filter off lead sulphate, barium sulphate, silica, and similar acid insoluble inert pigments. Separate as usual. (See above.) The filtrates should contain the titanium and zinc in solution as sulphates.

To the filtrate ammonia is added in excess, which precipitates the titanium with the iron group. For the complete separation of zinc from the iron group, the hydroxide precipitate should be re-dissolved in acid and a second precipitation with ammonia

should be made. Zinc may then be determined in the combined filtrate.

Titanium should be determined on a separate sample, as described in the above method for dry TiO_2 pigments.

*Antimony Oxide.** †—Antimony trioxide (Sb_2O_3) a fume pigment that has recently been introduced, may be occasionally found in certain classes of mixed paints. After being brought into solution, it may be quantitatively estimated by oxidation with permanganate or iodine. (See pages 27 and 28, Scott's Standard Methods of Chemical Analysis.)

SILICA OR SILEX—CHINA CLAY—ASBESTINE

These pigments, while all true silica pigments, are widely different from the standpoint of physical structure. A microscopic examination is of great value, showing silica or silex to consist of small, sharp particles, china clay to be tabloid in appearance and asbestine to consist of long, rod-like fibrous particles.

Moisture.—Heat 2 grams at 105° for two hours.

Loss on Ignition.—Ignite 1 gram to constant weight in a platinum crucible.

Insoluble Matter.—Boil 2 grams for thirty minutes with 50 cc. HCl (1:1), add 50 cc. of water, wash, ignite, and weigh insoluble residue.

In the case of china clay, or asbestine, a sodium carbonate fusion should be resorted to, with the subsequent dehydration of the silica.

The insoluble residue in either case is volatilized with H_2SO_4 and HF in the usual manner, any loss in weight being considered silica. Any residue is fused with sodium carbonate, the fusion being added to the original filtrate. Should $BaSO_4$ be present, the melt is digested with warm water, the $BaCO_3$ filtered off, washed, dissolved in hot dilute HCl and precipitated and determined as $BaSO_4$.

The filtrates, combined from the preceding filtrations, are examined for alumina, iron, manganese, calcium and magnesium in the usual way.

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* See "The evaluation of white pigments with special reference to antimony oxide," by H. E. Clarke, J. Oil & Colour Chemists' Assoc., Vol. 4, pp. 2-26 (1921); Chem. Abstrs., Vol. 15, p. 2197 (1921).

† See also Circulars 152 and 153 of Scientific Section for results of exposure tests.

Should it be necessary to determine the alkalies present, a separate sample is treated according to the J. Lawrence Smith method as described in Bulletin No. 700, U. S. Geological Survey.

Carbon Dioxide.—Determine by evolution with HCl, weighing in soda-lime, KOH solution, or by absorbing in $Ba(OH)_2$ solution and titrating or weighing as $BaCO_3$.

Any excess of calcium is reported as oxide. The magnesium is calculated as MgO, unless the carbon dioxide is in excess of the amount of calcium present, in which case it is reported as $MgCO_3$, and the remainder as MgO.

CALCIUM PIGMENTS

WHITING, PARIS WHITE, SPANISH WHITE, AND CHALK

These pigments are of the following composition:

Whiting.—The natural form of calcium carbonate.

Paris White.—The artificial form of calcium carbonate.

Gypsum.—The hydrated form of calcium sulphate, of formula $CaSO_4 . 2H_2O$.

These pigments are analyzed in the following manner:

Moisture.—Heat 2 grams at 105° C. for two hours.

*Total Soluble Lime.**—Weigh out 0.75 g. of the pigment into a small crucible, ignite cautiously to dull redness to destroy organic matter, cool, transfer to a 400-cc. beaker, add 20 cc. of H_2O, cover, then add 15 cc. of concentrated HCl and 3 or 4 drops of concentrated HNO_3, and boil till all the soluble matter is dissolved and all the CO_2 expelled. Wash off and remove the cover, dilute to about 150 cc. with freshly boiled H_2O, heat to boiling and add dilute NH_4OH (sp. gr. 0.96) carefully until a *slight* permanent precipitate forms. Heat to boiling and add 10 cc. of a 10-per-cent solution of oxalic acid; stir until the oxides of iron and aluminum are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 cc. of boiling H_2O and sufficient saturated solution of ammonium oxalate (20 to 25 cc.) to precipitate the lime. Boil and stir for a few moments, remove from the heat, let settle and filter on an 11-cm. filter. Wash 10 times with 10-to-15-cc. portions of hot water. Place beaker in which precipitation was made under the funnel, pierce apex of filter with stirring rod and wash precipitate into beaker with hot water, pour warm dilute H_2SO_4 (1:4) through paper and wash a few times; add about 30 cc. of

* Meade, "Portland Cement."

the dilute H_2SO_4 (1:4), dilute to about 250 cc., heat to 90° C. and titrate at once with standard $KMnO_4$ solution (solution should not be below 60° C. when end-point is reached). The $KMnO_4$ is best standardized against Bureau of Standards sodium oxalate.* Calculate to CaO and $CaCO_3$.

Mixed Calcium and Magnesium Carbonates.†—Weigh 1 g. of the finely powdered sample into a small porcelain dish, add 25 cc. of normal HCl, cover with a watch glass, and when effervescence has ceased, heat to boiling. Cool and titrate with normal NaOH solution, using methyl orange as indicator.

The calculation is as follows:

One gram CaO = 35.7 cc. of normal acid. CaO $\times$ 1.7844 = $CaCO_3$. Subtract number of cubic centimeters of NaOH required from 25; result gives number of cubic centimeters of normal acid corresponding to the $CaCO_3+MgCO_3$. Multiply the weight of CaO in 1 g. of sample (as found in preceding section on total soluble lime) by 35.7; product gives number of cubic centimeters of normal acid corresponding to the CaO present; subtract from total number of cubic centimeters of acid required by $CaCO_3+MgCO_3$ and multiply result by 0.042, obtaining weight of $MgCO_3$ in 1 g. of sample. The $MgCO_3$ determined by this process should not differ more than 0.25 per cent from that obtained by more elaborate methods. It is to be noted that this method is a measure of the total alkalinity, and if Ca or Mg are present in other forms than carbonate, a complete analysis would be necessary to give percentages of $CaCO_3$ and $MgCO_3$.

BARYTES AND BLANC FIXE

Of these two barium pigments used in the manufacture of paints, barytes is the natural barium sulphate, while blanc fixe is precipitated barium sulphate.

The following method may be used for the analysis of these pigments:

Moisture.—Heat 2 grams at 105° C. for two hours.

Loss on Ignition.—Ignite 1 gram to constant weight. The loss will be reported as loss on ignition, and will consist of free and uncombined water, carbon dioxide and organic matter.

Barium Sulphate.—Boil 1 gram with dilute HCl, evaporate to dryness, moisten with HCl, add water, boil, filter and wash. Should lead be present in the insoluble residue, as shown by the

* *Circular No. 40*, Bureau of Standards.

† J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," p. 522.

action of H_2S, treat the insoluble residue with a little (1 : 1) HCl and several drops of H_2SO_4. Filter, wash and weigh the residue. Treat the ignited residue with H_2SO_4 and HF, evaporate to dryness and ignite. The residue should show no loss as silica. The filtrate is examined for alumina, iron, calcium and magnesium in the usual manner.

Soluble Sulphates.—Treat 1 gram with 20 cc. conc. HCl, dilute to 200 cc. with hot water, boil, filter, wash, add NH_4OH until neutral, make acid with HCl and precipitate any sulphate as $BaSO_4$. Determine in the usual manner. Calculate to $CaSO_4$. If carbonates are present, calculate the remaining CaO to $CaCO_3$. Any excess of oxide is reported as CaO.

Carbon Dioxide.—Determine as outlined under silica. If any barium carbonate is present, it is determined in the filtrate from the preliminary HCl treatment, by precipitation and weighing, as $BaSO_4$. Any excess of carbon dioxide over the barium is reported as calcium carbonate.

ANALYSIS OF A COMPOSITE WHITE PAINT

A white paint may consist of a mixture of any of the preceding pigments, except that lead pigments and lithopone are seldom found together.

After separation from the oil and other liquids as outlined above, the white pigment mixture may be rapidly analyzed by the following method. It is, however, often advisable to resort to a qualitative examination before beginning the quantitative analysis. Also note method of analysis in interdepartmental specifications.

Insoluble Residue.—Boil 1 gram of the sample with 20 cc. (1 : 1) HCl. Evaporate to dryness, moisten the residue with a few cc. of concentrated HCl, allow to stand a few minutes, dilute with hot water, boil, filter and wash the insoluble residue thoroughly with hot water. Treat the insoluble residue with (1 : 1) HCl and 2 cc. H_2SO_4 to remove the last traces of lead. Filter, wash and weigh the insoluble residue. Determine the silica by volatilization with H_2SO_4 and HF. Any loss is reported as silica. Determine the $BaSO_4$ in the residue by boiling with dilute HCl or making a potassium bisulphate fusion. The residue remaining after either of these treatments is reported as barium sulphate.

Total Lead.—This constituent can be best determined on a separate sample. To 1 gram add 10 cc. of conc. HNO_3, boil, add,

after cooling, conc. H_2SO_4 and evaporate to strong SO_3 fumes. Dilute with water, allow to stand several hours, filter, wash slightly, dissolve and determine the lead volumetrically as outlined under Basic Sulphate White Lead.

Lead can also be determined in the combined filtrates from the insoluble residue. Precipitate the lead in an acid solution with H_2S and determine volumetrically in the above outlined manner.

To determine whether both sublimed white lead and corroded white lead are present, treat a separate portion of the paint with boiling acetic acid, filter and collect the insoluble residue. Determine the lead either in the filtrate or in the insoluble residue by the volumetric method. The lead soluble in acetic acid is the basic carbonate of lead and the lead oxide from the sublimed white lead, while the lead sulphate from the sublimed white lead remains insoluble.

Alumina and Iron Oxide.—Remove the H_2S from the filtrate by boiling, after removal of the lead, and precipitate the hydroxides in an ammoniacal solution after boiling with the addition of a few drops of HNO_3. Determine and separate in the usual manner.

Zinc.—Precipitate the zinc in the filtrate from the alumina and iron precipitation, after acidifying with acetic acid, and determine the zinc as outlined under Basic Sulphate White Lead.

Calcium and Magnesium.—Determine the calcium and magnesium in the filtrate from the precipitation of zinc sulphide in the usual manner, testing, however, first for the presence of barium.

Sulphate.—Determine as outlined under Zinc Lead and Leaded Zincs.

Sulphide.—Should lithopone be present, separate the zinc oxide and zinc sulphide as outlined under Lithopone.

Carbon Dioxide.—Determine as outlined under Silica.

Calculations.—Silica is reported as silica, except where alumina is present, showing the presence of china clay. In this case, calculate the alumina to clay by the method of Scott.

Weight of $Al_2O_3 + 2.5372 =$ weight of clay.

Weight of clay $\times 0.4667 =$ weight of SiO_2 in clay.

Any difference greater than 5% may be considered silica.

Barium sulphate is reported as barium sulphate or as lithopone, if zinc sulphide is present, according to the given composition of lithopone, 70% barium sulphate and 30% zinc sulphide.

Lead is reported as Basic Carbonate of Lead on the formula $2PbCo_3.Pb(OH)_2$.

Calculate lead soluble in acetic acid, after determining CO_2, to basic lead carbonate and any residual lead to lead oxide which, together with the lead sulphate, is reported as Sublimed White Lead.

Should calcium sulphate be present the portion soluble in water is examined for lime or sulphuric acid and calculated to calcium sulphate, any residual lime being calculated to calcium carbonate and any residual sulphuric acid being calculated to lead sulphate. Any residual CO_2 after calculating calcium carbonate is calculated to white lead and any residual lead is calculated to lead oxide.

Lead oxide should not be reported except in the presence of lead sulphate. Any large percentage of magnesium denotes the presence of asbestine.

See also Interdepartmental Specifications in back of volume.

CHAPTER XXVI.

ANALYSIS OF LEAD OXIDES

These pigments in the pure form are oxides of lead, of the generally accepted formula, Pb_3O_4, being probably mixtures of lead monoxide, and lead dioxide. In chemical composition they are the same, the proportions of lead monoxide and lead dioxide varying, however, but by their physical structure and color they can be readily differentiated.

Two methods are given for the analysis of this pigment.

Moisture.—Dry 2 grams at 105° for two hours.

Organic Color.—Boil 2 grams with 25 cc. of 95% ethyl alcohol, let settle, decant off the supernatant liquid; boil residue with water, decant as before and boil residue with very dilute NH_4OH. If either the alcohol, water or NH_4OH is colored, organic coloring matter is indicated.

Total Lead and Insoluble Residue.—Treat 1 gram with 15 cc. of HNO_3 (1 : 1) and sufficient hydrogen dioxide to dissolve all the PbO_2 on warming. If any insoluble matter is present, add 25 cc. of water, boil, filter and wash with hot water. Insoluble contains free SiO_2, and should be examined for $BaSO_4$ and silicates, if appreciable. To the original solution or filtrate from insoluble, add 20 cc. of conc. H_2SO_4 and evaporate to SO_3 fumes; cool and determine lead as lead sulphate either gravimetrically or volumetrically. If the sample contains soluble barium salts, the $PbSO_4$ will contain $BaSO_4$ and should be treated with acid-ammonium acetate solution, the lead being determined in the filtrate.

Determination of Lead Peroxide (PbO_2) and True Red Lead (Pb_3O_4). (Method of Diehl,* modified by Topf †—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)

Weigh 1 gram of finely ground sample into a 200-cc. Erlenmeyer flask, add a few drops of distilled water and rub the mixture to a smooth paste with a glass rod flattened on end. Mix in a small beaker 30 grams of C.P. "Tested Purity" crystallized sodium acetate, 2.4 grams of C.P. potassium iodide, 10 cc. of water and 10 cc. of 50% acetic acid; stir until all is liquid,

* Dingl. Polyt. Jour., 246, 196.

† Zeitschrift für analytische Chemie, 26, 296.

warming gently; if necessary add 2 to 3 cc. of H_2O, cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved; add 30 cc. of water containing 5 or 6 grams of sodium acetate, and titrate at once with decinormal sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off rod, add the sodium thiosulphate solution until pale yellow, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of thiosulphate that had been added.

Calculation.—The iodine value of the sodium thiosulphate solution multiplied by $0.94193=PbO_2$; the iodine value multiplied by $2.69973=Pb_3O_4$; the PbO_2 value multiplied by $2.86616=Pb_3O_4$.

Sodium Thiosulphate Solution (decinormal).—Dissolve 24.83 grams of C.P. sodium thiosulphate, freshly pulverized and dried between filter paper, and dilute with water to 1 liter at a temperature at which the titrations are to be made. The solution should be made with well-boiled H_2O, free from CO_2, or let stand eight to fourteen days before standardizing. Standardize with pure, resublimed iodine, as described in the chapter on Iodine, page 204, and also against pure potassium iodate. The two methods of standardization should agree within 0.1% on iodine value.

Starch Solution.—Two to 3 grams of potato starch are stirred up with 100 cc. of 1% salicylic acid solution, and the mixture boiled till the starch is practically dissolved and then diluted to 1 liter.

The second method for determination of the lead peroxide or true red lead content is somewhat shorter.

Treat 1 gram in a beaker with 15 cc. of nitric acid, sp. gr. 1.2 (110 cc. nitric acid sp.gr. 1.42 to 100 cc. of water). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 cc. of dilute hydrogen dioxide (1 part of 3% hydrogen dioxide to 3.5 parts of water). Add about 50 cc. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely

passed into solution, dilute with hot water to about 250 cc. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen dioxide solution must now be made.

Into a beaker pour 15 cc. of nitric acid of above strength and add exactly the same amount of hydrogen dioxide (10 cc.). Dilute to 250 cc. with hot water and titrate with standard potassium permanganate solution to a faint pink color.

The difference between the number of cc. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount required for the hydrogen dioxide which was reacted on by the red lead. The difference between the two amounts of potassium permanganate required multiplied by 3.058 grams gives the percentage of red lead present. The difference multiplied by 1.067 gives the percentage of PbO_2 present.

The latest methods for the examination of red lead and litharge, together with colorimetric measurements for the determination of copper and iron in pig lead, lead oxides, and lead carbonate, as furnished the writer by Dr. John A. Schaeffer, J. A. Calbeck and B. S. White, of The Eagle-Picher Lead Co., are given herewith.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF COPPER AND IRON IN PIG LEAD, LEAD OXIDES, AND LEAD CARBONATE*

Most methods in use for the determination of the small percentage of copper contained in pig lead, lead oxides and lead carbonate are long and tedious. This is especially true in those instances where refined metal serves as the base for the finished product and the copper content being extremely low, many difficulties present themselves; these can be overcome by the use of this colorimetric method.

While the estimation of the iron content in these compounds can be readily carried out colorimetrically by a separate analysis,† it has been found that the following method, which combines the determination of both copper and iron colorimetrically

* J. Ind. Eng. Chem., 7, 1035 (1915).
† J. Ind. Eng. Chem., 4, 659 (1912).

in one analysis, adds greatly to the rapidity and accuracy in finding the percentages of these impurities. The method not only eliminates the use of hydrogen sulphide, but it shortens the time of a single analysis to 30 to 40 minutes, while the results attain the same degree of accuracy as those established by the longer and more complicated methods.

The method of procedure varies somewhat with the nature of the sample to be examined: hence, it will be necessary to make especial mention of red lead.

ANALYSIS OF PIG LEAD, LITHARGE AND LEAD CARBONATE FOR COPPER

Weight of Sample.—In analyzing refined pig lead, or lead compounds made from refined metals, it is necessary, owing to the small percentages of copper and iron usually present, to use large samples. It has been found, by the use of this method, that smaller samples may be used with equally accurate results, thereby reducing the bulk to be handled and eliminating any errors which frequently result from the use of large volumes. A sample weighing 30 grams has been found sufficiently large for refined products, and not over 10 grams need be used for the crude or unrefined material.

Method of Procedure.—Weigh the finely divided sample into a 400-cc. beaker, and add small portions of hot (1 : 1) nitric acid until solution is effected. If any basic lead nitrate has been formed, dilute slightly with warm water and boil. Add 32cc. (1 : 1) sulphuric acid, stirring constantly while adding. Let the precipitate settle, and decant filtrate through a coarse filter paper. Wash four times by decantation, using small portions of warm, distilled water. Transfer the precipitate to the paper, wash again and allow to drain. Make the filtrate neutral with ammonium hydroxide and add 4 cc. excess. Boil for a short time and filter. Wash the precipitate well with warm water, and reserve for the determination of the iron. Render the filtrate acid with special c. p. hydrochloric acid, adding not more than two drops excess. Add six drops of (1:10) potassium ferrocyanide solution, filter through close filter papers using two to each funnel. Catch the filtrate and inspect for copper ferrocyanide. Let the precipitate drain well without washing. Dissolve the copper ferrocyanide off of the paper with alternate washings of small portions of ammonium hydroxide and hot water. Wash well and keep the bulk to 30 or

40 cc. Render slightly acid with hydrochloric acid, adding not over two drops excess. Transfer to a 100-cc. Nessler tube, and dilute to mark with distilled water. The copper is then determined colorimetrically according to a modification of the method of Carnelly.*

In another Nessler tube, place 10 cc. of 5 per cent ammonium nitrate solution, two drops concentrated nitric acid and 90 cc. distilled water, add from a burette graduated to tenths of 1 cc., standard copper sulphate solution until the color matches the sample under examination.

Standard Copper Sulphate Solution.†—"Dissolve 0.393 gram of pure $CuSO_4.5H_2O$, in one liter of distilled water. 1 cc. = 0.0001 gram of copper," or 0.00033 per cent when using a 30-gram sample.

Analysis of Red Lead for Copper.—Treat 30 grams of the sample with 40 cc. (1 : 1) nitric acid, using great care that the violence of the reaction does not cause the sample to froth over the beaker. Slowly add 30 to 40 cc. of 3 per cent hydrogen peroxide, stirring constantly. Boil until solution is effected, and proceed as directed above.

Sodium sulphite c. p. may be used in place of the hydrogen peroxide for effecting the solution of lead peroxide, adding it dry in small portions and boiling until no brown lead peroxide is present.

Determination of Iron in the Above Compounds.—For the iron determination, use the precipitate of iron hydroxide removed from the copper solution, proceeding as follows: Dissolve the precipitate contained on the paper with (1 : 1) hydrochloric acid, collecting the filtrate in a 300-cc. volumetric flask. Wash the paper free from acid with hot, distilled water, dilute to mark, and mix thoroughly. Place 10 cc. in a 100-cc. Nessler tube, add three drops nitric acid, 10 cc. (1:15) ammonium sulphocyanide solution, dilute to mark and compare with a standard iron solution.‡

The color is compared with a blank made in the following manner: A solution of ferric ammonium sulphate of known strength is required. This is made by dissolving 0.7022 gram of ferrous ammonium sulphate in water. Acidify with sul-

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* Sutton's Volumetric Analysis, p. 204.
† Sutton's Volumetric Analysis, p. 205.
‡J. Ind. & Eng. Chem., 4 (1912), 659.

phuric acid, heat to boiling and add a solution of potassium permanganate until all the iron is converted to the ferric condition. Only the very slightest pink tinge may be present after the addition of the potassium permanganate, as this tinge will fade away, while the presence of a pink color tends to vitiate the results. Allow the solution to cool and dilute to one liter. One cc. of this solution equals 0.0001 gram of iron.

Prepare the blank by pouring into a 100-cc. Nessler cylinder, 10 cc. ammonium sulphocyanide solution, and three drops of concentrated nitric acid. Dilute to 100 cc. and titrate to the exact color developed in the sample under examination, by the addition of the standard ferric ammonium sulphate solution. One cc. of this solution equals 0.01 per cent iron as the 10 cc. removed from the flask contained 1 gram sample. It will be found that the color can be accurately compared to within 0.001 per cent of iron content.

Comparison of Results on Copper.—Table XXX shows the results obtained by the above method, as compared with the method set forth by Fresenius,* on two sets of samples and a copper sulphate solution of known strength.

TABLE XXX—*Comparative Results (Percentages Cu) By Method of Fresenius and of Author*

No.	Pig Lead		Litharge and Red Lead		$CuSO_4$ Solution		
	Fres.	Color.	Fres.	Color.	Fres.	Color.	%Cu present
1	0.0009	0.00088	0.002	0.002	0.002	0.002	0.002
2	0.0013	0.0013	0.0008	0.0008	0.0008	0.0008	0.0008
3	0.0009	0.00088	0.0009	0.00088	0.00066	0.00066	0.0007
4	0.002	0.002	0.0007	0.0007	0.001	0.001	0.001
5	0.001	0.001	0.0015	0.0015	0.00066	0.00066	0.00066
6	0.0015	0.0015	0.0038	0.0038	0.0015	0.0015	0.0015
7	0.0012	0.0012	0.00088	0.00088	0.00088	0.00088	0.00088
8	0.0079	0.0079	0.00088	0.0009	0.0009	0.00088	0.0009
9	0.0013	0.0013	0.0013	0.0013	0.0015	0.0015	0.0015
10	0.0004	0.0004	0.00066	0.00066	0.0007	0.00066	0.0007

Precautions and Interfering Elements.—If the sample contains much zinc, the following method may be used for removing it: The filtrate from the iron precipitation, before precipitating the copper ferrocyanide, is rendered slightly acid with acetic

* Fresenius' Quantitative Chemical Analysis, Vol. II, p. 584.

acid, and 5 cc. of an 8 per cent sodium ammonium phosphate solution are added; boil, cool, filter and treat the filtrate as before outlined.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the colorimetric comparison of copper. If a faint white cloud of lead ferrocyanide should develop in the sample under examination, the addition of a small amount of very dilute lead nitrate solution to the standard will overcome this difficulty.

Reagents and Indicators.—This method presupposes the use of absolutely pure reagents, especially free from iron and copper. Use litmus paper as an indicator, as all other indicators, once introduced, will affect the final color.

RED LEAD AND ORANGE MINERAL

Schaeffer's Latest Method *

Moisture.—Dry 2 grams of the sample for 2 hours at 105° C. The loss will be moisture.

Red Lead, or Lead Dioxide.†—Treat 1 gram of the sample in a beaker with 15 cc. of nitric acid, specific gravity 1.2 (110 cc. nitric acid, specific gravity 1.42, to 100 cc. of water. This solution should be aerated to free it from all nitrous fumes).

Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 cc. of dilute hydrogen peroxide (1 part of 3-per-cent hydrogen peroxide to 3.5 parts of water). Add about 50 cc. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 cc. volume and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color. A blank titration on the hydrogen peroxide solution must now be made.

Titration of Hydrogen Peroxide, and Calculation of Results.—Into a beaker pour 15 cc. of nitric acid having the strength as above given and add exactly the same amount of hydrogen peroxide (10 cc.). Dilute to 250 cc. with hot water and titrate with standard potassium permanganate to a faint pink color.

The difference between the number of cubic centimeters of

* See *Chemical Analysis of Lead and Its Compounds.* Schaeffer, White and Calbeck. Pub. by The Eagle-Picher Lead Co., Joplin, Mo.

† J. Ind. Eng. Chem., 8, 237 (1916).

potassium permanganate required for the blank titration and the number required for the red lead titration is the amount of potassium permanganate required for the hydrogen peroxide which was reacted on by the lead dioxide. The difference between the two amounts of potassium permanganate required multiplied by 3.058 gives the percentage of red lead present according to the following proportion:

$$\text{Let } X = \%\ Pb_3O_4 \text{ per cc. difference}$$
$$2\,Fe : Pb_3O_4 :: 0.005 : X$$
$$112 : 685 :: 0.005 : X$$
$$X \text{ equals } 3.058$$

To determine the lead dioxide present multiply this difference by 1.067 according to the following proportion:

$$\text{Let } Y = \%\ PbO_2 \text{ per cc. difference}$$
$$2\,Fe : PbO_2 :: 0.005 : Y$$
$$112 : 239 :: 0.005 : Y$$
$$Y \text{ equals } 1.067$$

These calculations have been arranged in a series so devised as to permit the direct reading of the red lead percentage. The basis of the calculations depends on the fact that each cc. of potassium permanganate solution (iron value, 0.005) is equivalent to 3.058 per cent of true red lead; or, each 0.1 cc. is equivalent to 0.3058 per cent true red lead on a one-gram sample.

A red lead or orange mineral having 100-per-cent true red lead content requires 32.7 cc. potassium permanganate solution of the above strength.

The calculation, therefore, arranges itself as follows: Each 0.1 cc. on the selected burette represents 0.3058 per cent true red lead. The number 32.7 being equivalent to 100 per cent occupies an analogous position on the chart.

Calculations should be continued upward to 40.0 or to that point where the hydrogen peroxide solution used is of such strength that 10 cc. of the hydrogen peroxide solution require 40 cc. of the potassium permanganate solution. Calculations should be continued downward to 9.48 per cent true red lead content.

In using the series the chart is attached to the burette by a screw clamp. The blank determination is first made on the hydrogen peroxide solution and the value found is placed opposite zero on the burette. In the analysis of the red lead the value is then read off directly. As a hypothetical case we will

use a hydrogen peroxide solution with a blank titration of 34.1 cc. In the analysis of a red lead or orange mineral 4.2 cc. of the potassium permanganate solution is required for a final titration value. The calculation shows the difference between the two readings to be 29.9 cc. or multiplied by 3.058 equals a true red lead percentage of 91.43 per cent. Comparing this with the series of calculations we find 4.2 cc. from the 34.1 to be 91.43 per cent.

Should it be preferred to determine the lead peroxide content, the calculation will be based on the value 0.1067 for each 0.1 cc. of the potassium permanganate solution. It is understood that the division must be made to correspond to the 0.1 cc. divisions on the burette.

It is always advisable to make several blank determinations each day when this analysis is constantly made and when only occasionally used a blank titration should be made before each analysis.

The strength of the hydrogen peroxide solution will vary but the permanance of the permanganate solution renders the method accurate over a long period of time.

Standard Potassium Permanganate.—It is necessary to always have a potassium permanganate solution with an iron value of exactly 0.005 if the method described for red lead is used. Dissolve 5.75 grains c. p. salt in two liters distilled water and store in a brown bottle in a dark place for a week or more. By this time all organic matter will have been oxidized and after filtering the solution through an asbestos filter the solution is ready for standardization. As small amounts of MnO_2 destroy the permanence of this solution, it is necessary that it be removed by filtering. The method described in Bureau of Standards Circular No. 40 should be used. This method is as follows:

In a 400-cc. beaker, 0.25 gram of sodium oxalate is dissolved in 200 to 225 cc. of hot water (80-90° C.) and 10 cc. of (1 : 1) sulphuric acid added. The solution is at once titrated with the solution of permanganate, the solution being stirred continuously and vigorously. The permanganate must be added at the rate of 10 to 15 cc. per minute and the last 0.5 to 1 cc. must be added drop by drop, each drop being allowed to decolorize fully before the next is added. The solution should not be below 60° C. by the time the titration is completed. With a permanganate solution having an iron value of 0.005 per cc., 41.66 cc.

of the permanganate are required to react with 0.25 gram sodium oxalate.

If the first titration shows that the solution is too strong a small amount of distilled water should be added. To calculate exactly how much water to add divide 41.66 by the number cc. required in the titration and multiply by the number of cc. remaining in the bottle. The difference between this product and the number of cc. in the bottle will be the volume of water to add.

If the solution is too weak this difference multiplied by 0.00283 will be the grams of potassium permanganate salt to add. After the addition of water or salt the solution should again be titrated and if a titer of 41.66 is not obtained water or salt added until this titer is obtained. A solution carefully prepared in this manner should keep for months.

ANALYSIS OF FLAKE RED LEAD

SCHAEFFER METHOD

In certain instances it is found that flake red lead is soluble only with the greatest difficulty by the above procedure. In cases where this difficulty is encountered the following method will be found to give excellent results:

Digest 1 gram of the sample in a beaker with 15 cc. of nitric acid made up of a strength as given in the previous method. Boil the solution for a short time, add 10 cc. of a standard oxalic acid solution, the strength of which has been previously determined. Add 2 cc. of sulphuric acid (1 : 1). Boil the solution and titrate with a standard solution of potassium permanganate having an iron value of 0.005. A blank titration on the same amount of oxalic acid must be made. The difference between the amount of potassium permanganate required for the blank titration and that required for the red lead titration multiplied by the factor 3.058 or 1.067 will give the content of red lead or lead dioxide according to the proportions in the previous analysis.

Iron.—The iron should be determined colorimetrically as described under Red Lead.

Copper.—This constituent may be determined gravimetrically, or colorimetrically.

By the gravimetric method twenty grams of the sample are treated in a large beaker with 50 cc. nitric acid, 25 cc. of water and sufficient hydrogen peroxide to cause complete solution of the lead dioxide.

Determine the copper as outlined under the Analysis of Litharge.

The colorimetric method described under Red Lead is, however, more rapid and convenient.

Silica.—Silica is found to be present in oxides of lead both as free silica and as lead silicate, though usually in inappreciable amounts.

Digest 2 grams of the sample in a casserole with 2 grams of potassium chlorate and 15 cc. of dilute nitric acid. Proceed from this point as outlined under the Analysis of Litharge.

Organic Color.—The adulteration of red lead and orange mineral with organic coloring matter may be detected by adding 20 cc. of 95 per cent alcohol to 2 grams of the oxide, heating to boiling and allowing to settle. Pour off the supernatant liquid, boil with water, allow to settle and add a very small amount of ammonium hydroxide. If either the alcohol, water or ammonium hydroxide are colored, it indicates organic coloring matter. The quantitative determination is exceedingly difficult and the organic color is usually estimated by difference.

ANALYSIS OF LITHARGE

SCHAEFFER METHOD

Litharge, the monoxide of lead, PbO, may contain small percentages of iron, copper, silica, silver and free metallic lead. When the litharge has been made by a process where steam is used, there may be an appreciable amount of moisture present. It appears on the market in two colors, yellow and red. In some instances litharge is found containing a comparatively large percentage of red lead, which in certain uses is undesirable. The determination of each of the foreign constituents in litharge depends largely upon the use to which the litharge is to be put, as in very few cases are all the constituents determined.

Moisture.—Dry 2 grams of the sample at 105° C. for two hours. The loss will be moisture.

Free Metallic Lead.—Two grams of the sample are treated in a beaker with hot water and just sufficient acetic acid is slowly added, to dissolve the lead oxide. Stir the solution well and note whether any lead silicate remains undissolved. Should such remain, continue stirring until solution has been effected. The solution should never have greater than a 5-per-cent acetic acid strength.

Filter the solution and wash the residual metal three or four

times by decantation with hot water, having all the wash water pass through the filter paper, which is finally thoroughly washed with hot water. Transfer any metal on the filter paper to the beaker containing the residual lead, add 1 cc. of concentrated nitric acid and heat to solution. Dilute with 50 cc. of water, add 1 gram of sodium acetate and follow this with an excess of saturated neutral potassium bichromate solution, sufficient to precipitate all the lead. Boil, dilute to 100 cc., allow to cool, filter off the lead chromate, wash thoroughly and determine the lead chromate gravimetrically by drying at 100° C. or volumetrically by titration of the chromic acid present as outlined under the Analysis of Lead Ores. The factor for the direct determination of lead is, however, in this case 0.5, as a 2-gram sample is used.

Red Lead.—Determine the percentage of red lead present as outlined under the Analysis of Red Lead.

Iron.—Treat 1 gram of the sample with 10 cc. of water and just sufficient nitric acid, added drop by drop, to cause complete solution. Heat to boiling to oxidize all the iron and determinate it colorimetrically.

Copper.—Copper may be rapidly and accurately determined by the method described on page 186. The following gravimetric method, however, may be found more convenient if only a few determinations are to be made.

Twenty grams of the litharge contained in a 200-cc. flask are dissolved in nitric acid (50 cc. concentrated nitric acid to 100 cc. water). Boil to complete solution. Add 40 cc. of dilute sulphuric acid (1 : 1), boil gently for one hour and allow to cool. Filter off the lead sulphate and wash the precipitate thoroughly. Nearly neutralize all the free acid present with ammonium hydroxide, render slightly acid with hydrochloric acid, warm the solution and pass in hydrogen sulphide until no further precipitation of sulphide occurs. Filter off the precipitate without washing, using some of the filtrate to transfer the last traces of sulphide to the filter paper. Dissolve the precipitate in a little nitric acid and wash the filter paper thoroughly with hot water. Add 3 cc. of concentrated sulphuric acid, evaporate until the white fumes of sulphuric acid are evolved and allow the solution to cool. Add a little water and allow to stand for some hours. Filter off the lead sulphate, washing with hot water containing a little sulphuric acid.

Heat the filtrate to boiling and precipitate the copper as sul-

phide with hydrogen sulphide in an ammoniacal solution. Filter off the copper sulphide through an ashless filter paper, wash, ignite and weigh in a covered porcelain crucible, from which the heat and cover are occasionally removed for a few seconds.

The precipitate will consist of a mixture of CuO and Cu_2S. Since the percentage of copper is the same in both of these, the copper may be determined by multiplying the amount found by the factor 0.7988.

Silica.—Digest 5 grams of the sample in a covered casserole with 2 grams of potassium chlorate and 15 cc. of dilute nitric acid (1 : 1). Evaporate to dryness and dehydrate. Treat the residue, after cooling, with hot water and nitric acid. Heat to boiling, and filter the solution through an ashless filter paper. Wash the residue and filter paper thoroughly with hot acid ammonium acetate solution, made up to a strength as outlined under the Analysis of Lead Ores. Should the residue show a trace of iron, wash it thoroughly with dilute hydrochloric acid. Complete the washing with hot water, dry, ignite and weigh as SiO_2. The residue may be volatilized with hydrofluoric acid, if there is any doubt regarding the purity of the silica.

The silica is present as lead silicate and free silica. The above method determines the total content of silica. The free silica may be determined by dissolving the litharge in dilute nitric acid. Heat to boiling, filter, wash, ignite and weigh as silica.

CHAPTER XXVII.

ANALYSIS OF VERMILIONS

The following portion of Walker's* method, will suffice for the examination of Mercury Vermilion. Should the analyst desire to determine the sulphide of mercury present or make a more complete examination—reference may be made to the original method.

True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1%. Make the determination in a porcelain dish or crucible, using 2 grams of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury. Genuine mercury vermilion is at the present time little used in paints.

Organic Reds.—Organic lakes are used for most of the brilliant red, scarlet and vermilion shades. These organic coloring matters are sometimes precipitated on red lead, orange mineral or zinc oxide; but as a usual thing the base is barytes, whiting or china clay. Paranitraniline red, a compound of diazotized paranitraniline and beta-napthol, is largely employed; but a number of colors may be used. The examination of these reds follows the method as communicated to the writer by E. F. Hickson.

Percentage of Pigment in Paste or Paint—Weigh accurately about 15 g. of the paste or paint into a weighed centrifuge tube. Add 20 to 30 cc. of petroleum ether, mix thoroughly with a glass rod, wash the rod with more of the petroleum ether, and add sufficient of the reagent to make a total of 60 cc. in the tube. Place the tube in the container of a centrifuge, surround with water, and counter-balance the container of the opposite arm

* P. H. Walker, Miscellaneous Publications, No. 15, U. S. Bureau of Standards, p. 32.

with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice using petroleum ether. After drawing off the last extract, set the tube on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and keep in a stoppered bottle.

Analysis of Pigment.—Test the pigment first qualitatively. Place a small portion of the pigment in a 50 cc. beaker and add about 25 cc. of alcoholic KOH or NaOH. Para-red will turn a dark reddish purple. Pour off the colored solution, and repeat until all the color is in solution and a white base remains. Add a little HNO_3 to some of the base to show the presence of carbonate. A white base, giving no effervescence or test for CO_2, is probably composed of silicates or silicate and barium sulphate. Occasionally the base contains orange mineral; the addition of HNO_3 will turn this pigment brown and bleach out on adding a few drops of dilute $NaNO_2$ solution.

Percentage of color.—Weigh accurately about 0.5 g. portion of the pigment into a 250 cc. beaker, add about 100 cc. of warm chloroform, and stir with a glass rod, breaking up any lumps. Decant the colored solution through a weighed Gooch crucible, and leave the residue in the beaker. Add a 50 cc. portion of chloroform to the residue and stir well with a glass rod, breaking up any lumps. Decant the colored solution through the Gooch crucible and repeat the washing of the residue in the beaker with 50 cc. more of chloroform. Finally transfer the residue onto the Gooch crucible, and continue the washing with chloroform from a wash bottle until the base is white or the washings colorless. Dry the Gooch crucible at 105-110° C. to constant weight and report the loss as "pure color."

Note.—In case the examination of the pigment shows calcium carbonate to be absent and the base to be barium sulphate and silicates, a direct loss on ignition using 1 g of the sample will generally check the above within 0.5 per cent.

In case the base contains calcium carbonate, hydrated clays, alumina, etc., an ignition loss can not be calculated to organic color, since the results are too high, due to loss of combined water in the clay.

The above method for percentage of color will give in most cases a base free from organic color with about 250-300 cc. of chloroform.

Some samples have been washed with the following mixture for percentage of color and satisfactory results were obtained:

$$\left.\begin{array}{rl} 10 & \text{vol. ethyl ether} \\ 6 & \text{vol. benzol} \\ 4 & \text{vol. methyl alcohol} \\ 1 & \text{vol. acetone} \end{array}\right\} \text{Make alkaline with NaOH}$$

This is followed with alcoholic NaOH, alcohol and ether.

In separating the pigment from the vehicle, petroleum ether has been found to dissolve out only a slight amount of organic color.

CHAPTER XXVIII.

ANALYSIS OF INDIAN REDS, RED OXIDES

(PRINCE'S METALLIC, TUSCAN RED, ETC.)

Added Coloring Matter.—Test the pigment successively with hot water, 95 per cent ethyl alcohol, alcoholic NaOH or KOH and acetic acid. Chloroform, NaOH, H_2SO_4 HCl-stannous chloride, and other reagents may be tried.* The presence of an organic color may often be noted by the characteristic odor given off on ignition.

Loss at 100° C.—Heat 2 g. in a steam-jacketed oven at atmospheric pressure for three hours, or to constant weight.

Loss on Ignition.—Ignite a portion in a covered porcelain crucible to constant weight. This may include combined water, CO_2, organic matter, and some SO_3 if much $CaSO_4$ is present. CO_2 may be determined on a separate portion of the sample if desired.†

Free Acid or Alkali.—Boil 10 g. of sample with 100 cc. of water; filter and wash. Test filtrate with litmus paper; if acid, titrate with standard alkali and methyl orange and calculate to the equivalent of H_2SO_4. If alkaline, titrate with acid and calculate to the equivalent of Na_2O. Test filtrate for alkali salts and alkaline earths.

Insoluble, Iron Oxide, Etc.—Digest 2.5 g. of the sample (previously roasted at a low temperature if much organic matter is present; if very low in carbonaceous matter a little $KClO_3$ or $NaClO_3$ may be used in effecting solution) with 25 cc. of HCl (adding a little HNO_3 or chlorate, if not already added), wash off cover, and evaporate to dryness. Take up with HCl and water, filter, wash with dilute HCl and cold water. Make the filtrate up to 500 cc., mix, and examine as below.‡ Ignite the residue and weigh as "insoluble matter;"§ if this contains

* For details consult Zerr, "Tests for Coal-Tar Colors in Aniline Lakes," (English translation by C. Mayer); Schultz and Julius, "A Systematic Survey of the Organic Coloring Matters;" Hall, "The Chemistry of Paints and Paint Vehicles;" and Mulliken, "Identification of Pure Organic Compounds," *Commercial Dyestuffs*, Vol. III.

† It is inadvisable to use platinum unless it is known that attacking substances are absent.

‡ For more exact work this filtrate should be evaporated to dryness and SiO_2 removed.

§ If the insoluble contains appreciable amounts of Fe it will be necessary to fuse it with Na_2CO_3 or $K_2S_2O_7$ to determine total Fe in samples.

$BaSO_4$ it may be determined by fusing with six times its weight of Na_2CO_3, cooling, digesting with hot water, filtering, and washing the residue with hot water until free of sulfate.

Remove filtrate and place beaker used for the digestion underneath the funnel, pierce the filter with the glass rod, and wash the residue with a little water into the beaker; then pour hot dilute HCl (1:1) over paper, and finally wash with hot water. If necessary add more HCl to the beaker to dissolve the $BaCO_3$; heat to boiling, add dilute H_2SO_4 in slight excess, let stand about one hour on steam bath; filter, wash, dry, ignite, and weigh $BaSO_4$. (This subtracted from total insoluble will give "insoluble silicious matter," if it is desired to so report.) If it is desirable to analyze the insoluble silicious matter, this can be done by the usual methods for silicate analysis, but the results should be reported as a separate analysis.

For the determination of iron place 100 cc. of the first filtrate in a flask, add about 3 g. of granulated zinc, put a funnel into the neck of the flask, heat when the action slackens; if basic salts separate out add a few drops of HCl. When the reduction is complete, add 30 cc. of H_2SO_4 (1:2), and as soon as the residual zinc is dissolved, wash down the funnel inside and out and the neck of the flask with a fine jet of water, filling the flask (1000 cc.) about two-thirds full, cool in water, add 10 cc. of "titrating solution" (made by dissolving 160 g. of manganese sulfate in water, diluting to 1750 cc., adding 330 cc. of H_3PO_4, sp. gr. 1.72, and 320 cc. of concentrated H_2SO_4), and titrate with $KMnO_4$ (5.659 g. per liter) that has been standardized against Bureau of Standards sodium oxalate. Run a blank on the zinc, correct for same and calculate total iron as Fe_2O_3. Instead of adding the zinc to the solution, the reduction may be effected in a zinc reductor.*

The Fe_2O_3 may also be determined by the $K_2Cr_2O_7$ method.†

Lime.—Dilute an aliquot of 100 cc. of the original solution to about 200 cc., add 10 cc. of HCl, make alkaline with HN_4OH, add 2 or 3 cc. of bromine water, and boil till excess of NH_3 is expelled. Let settle, wash by decantation, redissolve in HCl, and reprecipitate with NH_4OH and bromine water. (Precipitate $= Fe_2O_3 . Al_2O_3 . TiO_2 . P_2O_5 . MnO_2$.) This precipitate may be ignited and weighed if desired.

To the combined filtrates add a few drops of NH_4OH, heat to

* Lord and Demorest, "Metallurgical Analysis," 1913, pp. 28-29.
† *Ibid.*, pp. 21-26.

boiling, and add an excess of saturated ammonium-oxalate solution; continue the boiling until the precipitate becomes granular, let stand about 30 minutes, filter, and wash with hot water till free of ammonium oxalate,* place beaker in which precipitation was made under the funnel, pierce apex of filter with stirring rod and wash precipitate into beaker with hot water, pour warm dilute H_2SO_4 (1:4) through paper and wash a few times; add about 30 cc. of H_2SO_4 (1:4), dilute to about 250 cc., heat to 90° C. and titrate at once with standard $KMnO_4$ solution (solution should not be below 60° C. when end-point is reached). Calculate to CaO. (The Fe value of $KMnO_4 \times 0.502 = CaO$.) The calcium-oxalate precipitate may be ignited to constant weight as CaO. If desired, magnesia may be determined as $Mg_2P_2O_7$ in the usual manner in the filtrate from the calcium oxalate.†

Soluble Sulfates.—Treat 1 g.‡ of the pigment (roasted gently if much organic matter is present) with 30 cc. of HCl, boil 10 minutes, add about 50 cc. of water, boil, filter, and wash with hot water. Heat the solution to boiling, add NH_4OH, filter and wash a few times with hot water; dissolve precipitate in hot dilute HCl and reprecipitate with NH_4OH, wash well with hot water. Render united filtrates just distinctly acid with HCl, boil, add by drops with stirring excess of 10 per cent $BaCl_2$ solution, boil about 10 minutes, filter on a Gooch crucible, wash with hot water, ignite and weigh as $BaSO_4$. Calculate to SO_3 or $CaSO_4$.

Total Sulfur other than that Present as $BaSO_4$.—Treat 5 g. of the sample in a covered porcelain dish with 50 cc. of aqua regia ($1HNO_3$: 9 HCl) and evaporate to dryness on steam bath. Add 20 cc. of concentrated HCl and about 250 cc. of water, make double NH_4OH precipitation; determine $BaSO_4$ as given under "Soluble Sulfates."

* For more exact work this precipitate should be dissolved in HCl and the calcium oxalate reprecipitated as above.

† If desired, a direct determination of Al_2O_3 may be made on an aliquot of the solution or on the HCl solution of the NH_4OH precipitate by Peters' phosphate method (this will include titanic acid) as described by Blair, "The Chemical Analysis of Iron," and Philips, "Methods of Iron Analysis Used in the Pittsburgh District."

‡ If low in soluble sulfates use a larger portion of sample.

CHAPTER XXIX.

ANALYSIS OF OCHERS

(SIENNAS, UMBERS, ETC.)

Loss at 100° C., loss on ignition, insoluble matter, total or soluble iron, alumina, lime and sulfur may be determined as outlined under the "Methods for Analysis of Indian Reds, etc.," using 1 g. or an aliquot corresponding to this weight.

Lead Chromate.—If present, the lead is removed in the above scheme by nearly neutralizing the filtrate from the insoluble matter with NH_4OH, cooling, and passing in H_2S, to precipitate PbS. Filter, wash with water containing H_2S, dissolve PbS in hot dilute HNO_3, add 10 cc. of concentrated H_2SO_4, evaporate till SO_3 is evolved, cool, dilute to 200 cc., let stand a few hours, filter on a Gooch crucible, wash with 1 per cent H_2SO_4, ignite, and weigh $PbSO_4$. Calculate to PbO or Pb. Heat the filtrate from the PbS to expel H_2S, oxidize with a little HNO_3, and make up to volume if working on more than 1 g.

The iron is best determined in an aliquot by the $K_2Cr_2O_7$ method. Another aliquot is treated with NH_4OH, the precipitate containing $Al_2O_3.Fe_2O_3.Cr_2O_3.P_2O_5.TiO_2$. Lime and MgO may be determined in filtrate.

The NH_4OH precipitate is dissolved in hot dilute HCl, washing paper with hot water, *cooled,* oxidized with Na_2O_2, boiled to expel H_2O_2, cooled, cover glass washed off, diluted to about 150 cc., and acidified with H_2SO_4. Add a measured excess of ferrous ammonium-sulfate solution—$(NH_4)_2Fe(SO_4)_2.6H_2O$, 12.4 g.; concentrated H_2SO_4, 50 cc.; and water to make 1 liter, and titrate back with standard $K_2Cr_2O_7$ solution, using $K_3Fe(CN)_6$ solution as an outside indicator. The $(NH_4)_2Fe(SO_4)_2$-$6H_2O$ solution is titrated with the $K_2Cr_2O_7$ solution to determine its value in terms of the latter. The Fe value of the $K_2Cr_2O_7$ solution $\times$ 0.5969 = CrO_3.

Or, moisten 1 g. of the pigment with water, add 5 cc. of concentrated HCl, boil a few minutes, *cool,* add Na_2O_2 in excess, boil to expel H_2O_2, cool, wash off cover glass, dilute, acidify with H_2SO_4, and titrate CrO_3 as above.

ANALYSIS OF VENETIAN RED

Analyze as given under "Methods for Analysis of Indian Reds, etc." Insoluble matter may be treated with HF and H_2SO_4 to determine SiO_2 by loss if desired.

ANALYSIS OF SIENNAS AND UMBERS

After gently roasting to destroy organic matter, test as given under "Methods for Analysis of Indian Reds, etc."

Manganese.—Manganese is determined by the bismuthate method.* Ignite gently (to destroy organic matter) 1 g. of the sample in a platinum dish, cool, add 10 cc. of water, 4 cc. of concentrated H_2SO_4 and about 20 cc. of HF (if necessary, add a little sulfurous acid). Evaporate until the H_2SO_4 fumes freely, cool and dissolve in 25 cc. of HNO_3 (1 part concentrated HNO_3 to 3 parts water). If no appreciable residue remains, transfer to a 100-cc. volumetric flask, using 25 cc. of HNO_3 (1 : 3) to rinse the dish, dilute to the mark with water, mix thoroughly. If there is an appreciable residue, filter on a small filter, wash with water, ignite residue in a platinum crucible, and fuse with a little sodium or potassium pyrosulfate. Dissolve in water, with the addition of a little HNO_3, add to the main filtrate, evaporate nearly to dryness, take up in HNO_3 (1: 3) and transfer to the flask as before. Pipette an aliquot of 10 cc. into a 200-cc. Erlenmeyer flask, add 30 cc. of water and 10 cc. of concentrated HNO_3, sp. gr. 1.4; add about 0.5 g. of sodium bismuthate, heat for a few minutes, or until the pink color has disappeared with or without the precipitation of MnO_2. Add a few small crystals of sodium or potassium nitrate to dissolve the MnO_2 and boil the solution several minutes to expel nitrous fumes (a little Na_2CO_3 will aid this). Add water to bring the volume up to 50 cc. and cool to about 15° C.; add about 0.5 g. of bismuthate and shake the flask well. Add 50 cc. of water containing 30 cc. of concentrated HNO_3 to the liter, filter by suction through an asbestos felt into a 300-cc. Erlenmeyer flask and wash with 50 to 100 cc. of the same acid. Run in a measured volume of standard ferrous ammonium-sulfate solution and titrate to a faint pink color with standard $KMnO_4$ solution. The number of cubic centimeters of the $KMnO_4$ solution obtained,

* Blair, "The Chemical Analysis of Iron."

subtracted from the number corresponding to the volume of ferrous solution used, will give the volume of $KMnO_4$ equivalent to the manganese in the sample, which, multiplied by the value of the $KMnO_4$ in Mn, gives the weight of manganese in the portion of sample used.

Standard $KMnO_4$ Solution.—The solution of $KMnO_4$ is composed of 1 g. dissolved in a liter of water. The Fe value of this solution $\times$ 0.1968 = Mn. This solution may be standardized against Bureau of Standards sodium oxalate (using about 0.05 to 0.1 g.) * Weight of $Na_2C_2O_4 \times 0.1639$ = Mn. Twelve grams of $(NH_4)_2Fe(SO_4)_2.6H_2O$, 25 cc. of concentrated H_2SO_4, and 25 cc. of H_3PO_4, sp. gr. about 1.7, are made up to 1 liter with water. The value of this solution should be determined against the $KMnO_4$ each day as follows:

Measure into a 200-cc. Erlenmeyer flask 50 cc. of HNO_3 (1: 3), cool, add a little bismuthate, dilute with 50 cc. of 3-per-cent HNO_3, filter by suction through an asbestos felt into a 300-cc. Erlenmeyer flask, and wash with 50 cc. of 3-per-cent HNO_3. Run in 25 cc. of the ferrous solution and titrate with $KMnO_4$ solution. Instead of titrating the permanganic acid formed by the bismuthate with the ferrous solution and then titrating back with $KMnO_4$, a direct titration with standard sodium arsenite solution may be made.†

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* W. Blum, "Original Communications," Eighth International Congress of Applied Chemistry," Vol. I, pp. 61-85.

† Lord and Demorest, "Metallurgical Analysis," 1913, p. 82.

CHAPTER XXX.

ANALYSIS OF YELLOW AND ORANGE PIGMENTS

CHROME YELLOWS, AMERICAN VERMILION, BASIC LEAD CHROMATE

A pure chrome yellow should contain only lead chromate and other insoluble lead compounds.

Added Coloring Matter.—Test the pigment successively with hot water, 95-per-cent ethyl alcohol, and chloroform. The solutions should remain colorless. Other reagents may be tried.*

Moisture.—Heat 2 g. at 105° C. for two hours. The loss in weight is reported as moisture.

Insoluble Matter.—Treat 1 g. with 25 cc. of concentrated HCl and boil for from 5 to 10 minutes in a covered beaker, adding about 6 drops of alcohol to the boiling liquid, one at a time. Dilute to 100 cc. with hot water and boil for from 5 to 10 minutes (the solution should be complete). Filter the hot solution (if insoluble matter is present) and wash with boiling water till washings are free from lead and chlorine. Ignite the insoluble matter, weigh, and examine for SiO_2, $BaSO_4$, and Al_2O_3.

Total Lead.—Nearly neutralize with NH_4OH the filtrate from the insoluble matter (or the original solution), dilute to about 300 cc., and pass into the clear solution a rapid current of H_2S until all of the lead is precipitated as PbS. Let the precipitate settle, filter, wash with water containing some H_2S. Boil the filter and precipitate with dilute HNO_3 until all of the lead has dissolved, filter, and wash thoroughly with hot water. To the filtrate, add 10 cc. of H_2SO_4 (1:1), evaporate until copious fumes of SO_3 are evolved, cool, add about 75 cc. of H_2O and then 75 cc. of 95-per-cent ethyl alcohol. Let stand about one hour, filter on a Gooch crucible, wash with dilute alcohol, dry, ignite, and weigh as $PbSO_4$.

Chromium (*Iron, Aluminum*).—Heat the filtrate from the PbS to expel H_2S and, if iron is present, add a few drops of HNO_3 and boil about two minutes. Render the solution just alkaline with NH_4OH, boil a few minutes, filter, and wash with hot 2-per-cent NH_4Cl solution. (If the sample contains an

* For details consult Zerr, "Tests for Coal-Tar Colors in Aniline Lakes" (English translation by C. Mayer); Schultz and Julius, "A Systematic Survey of the Organic Coloring Matters;" Hall, "The Chemistry of Paints and Paint Vehicles;" and Mulliken, "Identification of Pure Organic Compounds," *Commercial Dyestuffs*, Vol. III.

appreciable amount of zinc, a double precipitation should be made.) In the absence of iron and aluminum this precipitate may be ignited and weighed as Cr_2O_3. If iron and aluminum are present, dissolve the NH_4OH precipitate with hot dilute HCl, washing the paper with hot water; *cool,* add NH_4OH until alkaline, and then add Na_2O_2 (about 1 g.), keeping the beaker covered. Digest until all of the chromium and aluminum have been dissolved, adding more Na_2O_2 if necessary. Filter off the $Fe(OH)_3$, wash thoroughly with hot water, ignite and weigh as Fe_2O_3; or, dissolve the precipitate in HCl and determine the Fe content volumetrically. Make up the filtrate from the $Fe(OH)_3$ to 250 cc. in a graduated flask, and mix. Render an aliquot portion acid with H_2SO_4, boil to expel any free oxygen, cool, add an excess of standard $(NH_4)_2Fe(SO_4)_2.6H_2O$ solution and titrate back with N/10 $K_2Cr_2O_7$ solution, using $K_3Fe(CN)_6$ as outside indicator. (The CrO_3 may also be determined by acidifying the aliquot portion with acetic acid, precipitating as $PbCrO_4$ or $BaCrO_4$, and finally weighing on a Gooch crucible.) To determine Al_2O_3, make an aliquot portion of the filtrate from the $Fe(OH)_3$ acid with HCl, and then just distinctly akaline with NH_4OH, heat to boiling, let settle, filter, wash with hot 2-per-cent NH_4Cl solution, ignite and weigh as Al_2O_3. If iron and aluminum are not to be determined or are present in negligible amounts, the first NH_4OH precipitate may be dissolved in dilute HCl, oxidized with Na_2O_2, acidified with H_2SO_4, boiled, and CrO_3 determined volumetrically. The CrO_3 in the absence of other oxidizing substances, may be determined on 1 g. of the pigment by Schwartz' method (Fresenius Quantitative Chemical Analysis, Ed. 6, Vol. 1, p. 424).

Zinc, Calcium, and Magnesium.—Precipitate any zinc in the filtrate from the first NH_4OH precipitate with H_2S, filter, wash with dilute $(NH_4)_2S$, dissolve the zinc sulfide in dilute HCl, and determine the Zn content volumetrically by $K_3Fe(CN)_6$ method. In the filtrate from the zinc sulfide, determine calcium by the oxalate method and magnesium as $Mg_2P_2O_7$.

Sulfuric Anhydride.—Heat 1 g. of the pigment with 10 cc. of concentrated HCl until free chlorine is expelled, add about 300 cc. of water and boil; filter off any insoluble matter and wash thoroughly with hot water, heat to boiling, and precipitate with $BaCl_2$ solution in the usual manner. Keep the solution hot while filtering off the $BaSO_4$ and wash with hot water until the washings show no lead or chlorine.

Carbon Dioxide.—Determine carbon dioxide by the evolution method, using dilute HNO_3, free from oxides of nitrogen.

Water-Soluble Matter.—Weigh 5 g. of the pigment on to a weighed Gooch crucible (containing asbestos, and dried at 110° C.), wash six times with 25-cc. portions of cold water; dry at 110° C. and weigh. The loss in weight, corrected for moisture (as determined above), represents the soluble salts removed by the water. The washing may be examined, if desired.

Calculations.—Calculate CrO_3 to $PbCrO_4$, and SO_3 to $PbSO_4$ if calcium is absent. If CO_2 is present and calcium and mannesium are absent, calculate to $(PbCO_3)_2.Pb(OH)_2$. Report any residual Pb as PbO. If calcium is present, calculate to $CaCO_3$ if CO_2 is also present. If calcium and SO_3 are present and CO_2 is absent, calculate to $CaSO_4$. If calcium, CO_2, and SO_3 are present, calculate to $CaCo_3$; any residual calcium is then calculated to $CaSO_4$. Report zinc as ZnO.

CHAPTER XXXI.

ANALYSIS OF BLUE PIGMENTS

IRON CYANIDE BLUES. (PRUSSIAN BLUE, CHINESE BLUE, ANTWERP BLUE, MILORI BLUE, BRONZE BLUE, STEEL BLUE.)

The analysis of these blues, as is generally the case with pigments, does not necessarily give results which can be used to grade samples, the strength and color tests being most important.

Moisture.—Heat 2 g. of the pigment at 105° C. for two hours. The loss in weight is reported as moisture. A "dry" Prussian blue should contain less than 7 per cent of moisture.

Insoluble Matter.—Ignite 1 g. of the pigment in a porcelain dish at a low temperature, just high enough to decompose the last trace of blue, but not high enough to render the iron difficultly soluble in HCl. Cool, add 15 cc. of HCl and a few drops of bromine, cover with a watch-glass, and digest on the steam bath; wash off cover, evaporate to a syrup, add water, boil, filter, wash with hot water, ignite the residue and weigh. Examine the insoluble residue for silica, barium sulfate, and alumina. A pure Prussian blue should show no insoluble residue.

Iron and Aluminum.—Determine iron and aluminum in the filtrate from the insoluble matter by precipitation with NH_4OH in the usual manner. A double precipitation is desirable. Ignite and weigh $Fe_2O_3+Al_2O_3$, deduct Fe_2O_3 (calculated from total Fe), and calculate Al_2O_3 to Al.

Calcium.—Determine calcium in the filtrate from the Fe_2O_3 $+Al_2O_3$ by precipitation with ammonium oxalate; titrate with $KMnO_4$, or, ignite and weigh as CaO. Acidify the filtrate from the calcium oxalate with HCl and dilute to a definite volume and mix.

Sulfuric Acid.—Determine sulfuric acid in an aliquot of the above solution as $BaSO_4$ in the usual manner.

Alkali Metal and Alkaline Salts.—Evaporate an aliquot of the above solution with sulfuric acid, ignite (treating with solid ammonium carbonate), and weigh. Determine whether the alkali metal is sodium or potassium and subtract the alkali metal corresponding to the sulfate (SO_4) found. The remainder is alkali combined with the blue and is reported as Na or K.

Total Iron.—Decompose and dissolve 1 g. of the pigment as

under "Insoluble Matter," reduce, and determine the total iron with $KMnO_4$ or $K_2Cr_2O_7$. There should be not less than 30 per cent, calculated on the dry pigment.

Total Nitrogen.—Determine the total nitrogen on a 1-g. sample of the pigment by the Kjeldahl-Gunning Method, digesting for at least 2½ hours. The sulfuric acid should not blacken, which would indicate organic adulteration.

Water-Soluble Matter.—Weigh 2.5 g. of the pigment into a graduated 250-cc. flask, add 100 cc. of water, and boil for five minutes. Dilute with water, let stand until at room temperature, make up to mark, mix and let settle. Filter through dry paper and discard the first 25 cc. Transfer 100 cc. of the clear filtrate to a weighed dish, evaporate to dryness on a steam-bath, dry in an oven at 105° C. for 30 minutes, cool and weigh.

Calculations.—The percentage of Prussian blue may be obtained with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 4.4 or the percentage of iron (in the absence of other iron pigments) by 3.03.*

Note.—Some blues, *e. g.*, Chinese blue, may contain tin salts. Others may contain manganese or chromium compounds. The presence of these compounds should be determined by a qualitative examination at least.

Heckel Method for Iron in Prussian Blue.—In a method for the examination of Prussian blue, worked out by James E. Heckel, the sample is heated in an open crucible, gently at first and later with strong heat. The contents of the crucible are then brushed into a beaker, also placing the crucible in the beaker if any of the Fe_2O_3 clings to it. Heat with 25 cc. concentrated HCl and add 3 cc. $SnCl_2$. In about fifteen minutes solution is complete. If the crucible has been placed in the beaker, remove it after rinsing with distilled water into the beaker, and transfer the solution to a 500-cc. flask, washing out all $FeCl_3$ from beaker. Make up to mark with distilled water. Concentrate a 100-cc. aliquot portion and reduce with $SnCl_2$. Stir constantly, adding the material, drop by drop, from a burette until apple-green color is produced—from chrome-oxidized blues. For chlorate-oxidized blues, the $SnCl_2$ is added until complete disappearance of the yellow color. At once pour in 50 cc. cold $HgCl_2$ and 50 cc. $MnSO_4$, dilute with cold distilled water to about 600 cc. and titrate with $KMnO_4$. For those interested in this method, see files of Drugs, Oils and Paints.

* Parry and Coste, *The Analyst*, Vol. 21, pp. 225 to 230 (1896).

ANALYSIS OF ULTRAMARINE BLUE

An analysis is of little value for determining the quality of pure ultramarines, but is useful in the identification of foreign admixtures. Practical tests as to the stability and compatibility of the pigment in mixtures with other pigments, coloring power, tint, fineness, fastness to light, etc., are more important than chemical analysis.

Moisture.—Heat 2 g. of the pigment at 105° C. for two hours, cool and weigh. The loss in weight is reported as moisture.

Silica.—Treat 1 g. of the pigment in a covered dish or casserole with 30 cc. of HCl (1 : 1), heat until decomposed, wash off and remove cover, and evaporate to dryness on the steam-bath. Moisten with concentrated HCl and again evaporate to dryness, add 1 to 2 cc. of concentrated HCl, let stand about 5 minutes, add hot water, filter and wash the insoluble matter with hot water. If great accuracy is desired, evaporate the filtrate to dryness, take up with HCl and water, filter on a second paper, wash, and add the residue to the main insoluble. Ignite the insoluble matter, cool and weigh. Determine SiO_2 by volatilization with H_2SO_4 and HF. Make a qualitative examination of any residue that may remain.

Alumina.—Render the filtrate from the silica faintly alkaline with NH_4OH, boil a few minutes, filter, wash with hot 2-per-cent NH_4Cl solution, ignite and weigh as $Al_2O_3(+Fe_2O_3)$. For more accurate work, dissolve the $Al(OH)_3$ precipitate in HCl and reprecipitate as above.

Sodium Oxide.—Acidify the filtrate from the Al_2O_3 with H_2SO_4, evaporate to dryness, ignite (finally adding solid ammonium carbonate) and weigh as Na_2SO_4. Calculate to Na_2O. If calcium is present it should be precipitated with ammonium oxalate in the filtrate from the Al_2O_3, ignited and weighed as CaO, and the sodium determined in the filtrate from the calcium oxalate, as described.

Total Sulfur.—Mix 1 g. of the ultramarine with 4 g. of Na_2CO_3 and 4 g. of Na_2O_2 in a nickel crucible, cover with about 1 g. of Na_2CO_3 and fuse, using an aluminum or asbestos shield to prevent the sulfur being taken up from the gas. Dissolve the fused mass in dilute HCl, filter and wash, if necessary (there should be no insoluble residue), precipitate with $BaCl_2$ and determine total sulfar by weighing as $BaSO_4$. Calculate to S.

Sulfur Present as Sulfate.—Dissolve 1 g. of the pigment in dilute HCl, boil to expel H_2S, and filter if necessary; make the solution faintly alkaline, with NH_4OH and just distinctly acid

with HCl, and treat with $BaCl_2$ in the usual manner. Calculate $BaSO_4$ to SO_3 and to S.

Sulfur Present as Sulfide.—Subtract the sulfur present as sulfate from the total sulfur.

ANALYSIS OF COBALT BLUE

This pigment is essentially a compound of the oxides of aluminum and cobalt.* Certain shades of ultramarine blues are often sold under the name "cobalt blue."

Moisture.—Heat 2 g. of the pigment at 105° C. for 2 hours. The loss in weight is reported as moisture.

Alumina.—Fuse 1 g. of the pigment with 12 to 15 g. of sodium or potassium pyrosulfate, cool, digest with water and HCl, filter, and wash the residue with hot water. Make the filtrate up to 250 cc. in a graduated flask and mix. Ignite the residue, cool, weigh, and examine for SiO_2 and $BaSO_4$. Dilute an aliquot portion of the filtrate to 200 cc., add 5 g. of NH_4Cl, heat to boiling, and add dilute NH_4OH till just distinctly alkaline (a few drops of 0.2-per-cent alcoholic solution of methyl red is recommended as indicator). Boil for one or two minutes, filter at once, dissolve the precipitate with HCl, and reprecipitate as before. Filter, wash thoroughly with hot 2-per-cent NH_4Cl (or NH_4NO_3) solution, ignite, and weigh as Al_2O_3.

Calcium and Magnesium.—Unite the filtrates from the Al_2O_3, saturate with hydrogen sulfide, filter, and determine calcium and magnesium in the filtrate in the usual manner.

Cobalt Oxides.—Subtract the determined constituents from 100 and report the difference as cobalt oxides, unless a qualitative examination shows the presence of other substances in significant amounts. Should the pigment contain phosphoric acid (or arsenic acid) in more than negligible amounts, these must be removed before determining aluminum, calcium and magnesium.†

ANALYSIS OF SUBLIMED BLUE LEAD‡

BASIC SULPHATE—BLUE LEAD

Total Lead.—The total lead content is determined by the volumetric method for lead as outlined under Basic Sulphate-White Lead.

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* "Analysis of Paint and Varnish Products," C. D. Holley, p. 210 (1912).

† See "Technical Methods of Chemical Analysis," Lunge-Keane, Vol. III, Part II, p. 978 (1914).

‡ "The Chemical Analysis of Lead and its Compounds," Schaeffer and White, pp. 22-24.

Total Sulphur.—Treat 0.5 gram with 10 cc. of water and a few cc. of bromine water. Boil gently until all the bromine has passed off. Dilute with water, add another portion of bromine water, boil, and continue the treatment until the sediment has become white in color. Add 8 cc. of nitric acid, evaporate until the brown fumes of nitric acid have disappeared, dilute with water and add an excess of sodium carbonate. Determine as outlined under Basic Sulphate-White Lead.

Lead Sulphate.—On a separate sample determine the lead sulphate as outlined under Sublimed White Lead, by transposition of the sulphate with sodium carbonate.

Lead Sulphite.—Boil one and one-half grams of the sample with 3 grams of sodium carbonate, allow to stand, filter and thoroughly wash. To the filtrate add 3 cc. of bromine water, heat gently to oxidize the sodium sulphite to sulphate, acidify with HCl and precipitate the sulphate with barium chloride. Filter, wash and weigh in the usual manner. The barium sulphate formed will contain both the sulphur present as sulphate and that present as sulphite converted to sulphate. Deduct the amount present as sulphate and calculate the remainder to lead sulphite.

Lead Sulphide.—Deduct the sulphur present as sulphate and sulphite from the total sulphur and report the difference as lead sulphide.

Lead Carbonate.—A small amount of lead may be present as carbonate. Determine the carbonic acid present as outlined under Basic Carbonate White Lead, and calculate this carbonic acid to lead carbonate.

Lead Oxide.—Deduct the lead present as lead sulphate, lead sulphite, lead sulphide and lead carbonate from the total lead and report the difference as lead oxide.

Zinc Oxide.—Determine the zinc present as outlined under Sublimed White Lead, and report it as zinc oxide.

Carbon and Volatile Matter.—Ignite the sample in a partially covered crucible at a low heat for two hours. Report the difference as carbon and volatile matter.

CHAPTER XXXII.

ANALYSIS OF GREEN PIGMENTS
(CHROME GREEN)

A pure chrome green should contain only Prussian blue and pure chrome yellow. A microscopic examination should be made to determine whether the green is a combined precipitation product, which is of the greater value, or one mixed after separate precipitation. A good green will show the presence of green and blue particles, while a poor green will show yellow and blue particles mixed with green.

Moisture.—Heat 2 g. of the pigment at 105° C. for two hours. The loss in weight is reported as moisture.

Insoluble Matter.—Heat gently 1 g. of the pigment in a small porcelain dish until the blue color has been decomposed. The heating should be carried out very carefully so as not to render the iron difficultly soluble. (With some very pure chrome greens it may be advantageous to mix the sample with 2 to 5 times its weight of pure barium sulfate before igniting.) Let cool, transfer to a beaker, and determine insoluble matter as outlined in Section 5 for Yellow Pigments.

Lead.—Determine lead in the filtrate from the above as outlined in Section 6 for Yellow Pigments.

Iron, Alumina and Chromium.—Determine iron, aluminum and chromium in the filtrate from the PbS as outlined for Yellow Pigments, making a double precipitation.

Zinc, Calcium, and Magnesium.—Determine zinc, calcium and magnesium in the filtrate from the iron, aluminum and chromium determination as outlined for Yellow Pigments.

Carbon Dioxide.—Determine carbon dioxide by the evolution method, using dilute HNO_3 (1 : 5).

Sulfuric Anhydride.—Heat gently 1 g. of the pigment, cool, transfer to a beaker, add 30 cc. of concentrated HCl, cover, and heat on a steam-bath for about 30 minutes (in some cases, the iron compounds will go into solution more readily by letting the solution stand for some time at room temperature and then heating). Wash off cover, add 50 cc. of boiling water, boil for five minutes, filter, render the filtrate faintly alkaline with NH_4OH, then slightly acid with HCl, heat to boiling, and precipitate with $BaCl_2$ (15 cc. of 10-per-cent solution)

in the usual manner, boiling about ten minutes. Filter, wash with hot water, ignite, and weigh the $BaSO_4$.

Nitrogen.—Determine nitrogen on a 1-g. portion of the pigment by the Kjeldahl-Gunning Method, digesting for at least 2½ hours.

Water-Soluble Matter.—Weigh 2.5 g. of the pigment into a graduated 250-cc. flask, add 100 cc. of water, and boil for five minutes. Dilute with water, let stand until at room temperature, make up to the mark, mix, and let settle. Filter through dry paper and discard the first 25 cc. Transfer 100 cc. of the clear filtrate to a weighed dish, evaporate to dryness on a steam-bath, dry in an over at 105° C. for 30 minutes, cool and weigh.

CHAPTER XXXIII.

ANALYSIS OF BLACK PIGMENTS

The black pigments include those which contain carbon as their essential constituent. The introduction of asphaltic and coal-tar mixtures complicates their chemical analysis. For those pigments which contain coal-tar mixtures, recourse may be had to works * covering this matter thoroughly.

The analysis of the simple black pigments may be carried out in the following way:

Moisture.—Dry 2 grams at 105° C. for two hours.

Oil.—Extract 2 grams, with ether in a fat-extraction apparatus.

Carbon.—Determine the carbon by difference after determining the moisture, oil and ash. For an exact determination of carbon make a combustion test, absorbing the carbon dioxide in soda-lime or caustic potash as usual.

Ash.—Ignite 2 grams to a bright red heat until all the carbon is driven off. If graphite is present, the ignition should be carried out with the aid of oxygen. Should carbonate be present, mix the ash with a small amount of ammonium carbonate and again ignite, thus reconverting to carbonate any oxide which may have been formed.

Analysis of Ash.—The ash is boiled with concentrated HCl and the insoluble residue determined in the usual manner. The filtrate is examined for calcium, magnesium and phosphoric acid.

Calculate the magnesium to phosphate, any residual phosphoric acid to calcium phosphate and any residual calcium to carbonate.

Gases.—Black pigments such as lamp or gas blacks may contain as high as 15 per cent absorbed or adsorbed gases. High vacuum is necessary to free such gases from the pigment.

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* Allen's "Commercial Organic Analysis," 4th Edition; "The Analysis of Paints," Gardner and Schaeffer.

INDEX

For analysis and physical tests on paints, varnishes, colors and pigments, also see interdepartmental specifications in back of volume.

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For analysis and physical tests on paints, varnishes, colors and pigments, also see interdepartmental specifications in back of volume.

INTERDEPARTMENTAL COMMITTEE

STANDARD SPECIFICATIONS BOARD

UNITED STATES GOVERNMENT

The circulars issued to date, in so far as they are available at the Printing Office, have been bound in this volume. The list of circulars is given below:

No.—82 2nd ed. Linseed Oil.
No.—84 2nd ed. Basic Carbonate White Lead.
No.—85 2nd ed. Basic Sulphate White Lead.
No.—87 2nd ed. Zinc Oxide.
No.—88 2nd ed. Leaded Zinc Oxide.
No.—89 2nd ed. White and Tinted Paints (exterior).
No.—90 2nd ed. Red Lead.
No.—91 2nd ed. Ochers.
No.—93 2nd ed. Iron Oxide.
No.—94 2nd ed. Black Paint.
No.—97 3rd ed. Green Paint.
No.—103 2nd ed. Spar Varnish.
No.—111 2nd ed. Interior Lithopone Paint.
No.—117 2nd ed. Interior Varnish.
No.—86 1st ed. Turpentine.
No.—98 1st ed. Mineral Spirits.
No.—102 1st ed. Composite Thinners.
No.—105 1st ed. Liquid Paint Driers.

Circular 86 has not yet been reprinted as a second edition. When printed, the only change will be the lowering of the minimum limit for the refractive index for wood turpentine from 1.468 to 1.465, and the lowering of the minimum refractive index of the residue of wood turpentine after polymerization, from 1.495 to 1.480.

In the second edition of 98, which is not yet printed, a more rigid sulphur test may be introduced. The committee is now working with the petroleum committee of the Federal Specification Board on this matter. The new test will probably be the copper strip test.

In circulars 102 and 105 any slight changes made in the second edition will be matters of form rather than of substance, and of a minor nature.

H. A. G. Sept. 15, 1922.

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS
No. 82

[2d edition. Issued June 8, 1922]

UNITED STATES GOVERNMENT SPECIFICATION FOR LINSEED OIL, RAW, REFINED, AND BOILED

FEDERAL SPECIFICATIONS BOARD

STANDARD SPECIFICATION No. 4

This Specification was officially adopted by the Federal Specifications Board, on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS

1. GENERAL

Linseed oil, raw, refined, or boiled, as specified in contract, shall be pure and shall conform to the following requirements:

RAW LINSEED OIL

	Maximum	Minimum
Loss on heating at 105 to 110° C (per cent)	0.2	
Foots by volume (per cent)	2.0	
Specific gravity 15.5/15.5° C	.936	0.932
Acid number	6.0	
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.5	
Iodine number (Hanus) [a]		170.0
Color	Not darker than a freshly prepared solution of 1.0 g potassium bichromate in 100 cc pure strong (1.84 specific gravity) sulphuric acid.	

[a] When raw linseed oil from North American seed is specified by the purchaser, the iodine number must be not less than 180 and the oil shall conform to all the other requirements as above.

REFINED LINSEED OIL

Contract shall state whether acid refined or alkali refined is desired.

	Maximum	Minimum
Loss on heating at 105 to 110° C (per cent)	0.2	....
Foots by volume (per cent)	.2	....
Specific gravity at 15.5/15.5° C	.936	0.932
Acid number (acid refined oil)	9.0	3.0
Acid number (alkali refined oil)	3.0	....
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.5	....
Iodine number (Hanus) [a]	....	170.0
Color	Not darker than a freshly prepared solution of 0.1 g potassium bichromate in 100 cc pure strong (1.84 specific gravity) sulphuric acid.	

[a] When refined linseed oil from North American seed is specified by the purchaser, the iodine number must be not less than 180 and the oil shall conform to all the other requirements as above.

BOILED LINSEED OIL

Boiled oil shall be pure, well-settled linseed oil that has been boiled with oxides of manganese and lead. It shall conform to the following requirements:

	Maximum	Minimum
Loss on heating at 105 to 110° C (per cent)	0.2	....
Specific gravity at 15.5/15.5° C	.945	0.937
Acid number	8.0	....
Saponification number	195.0	189.0
Unsaponifiable matter (per cent)	1.50	....
Iodine number (Hanus) [a]	....	168.0
Ash (per cent)	.7	.2
Manganese (per cent)	....	.03
Lead (per cent)	....	.1
Time of drying on glass (hours)	20.0	....

[a] When boiled linseed oil from North American seed is specified by the purchaser, the iodine number must be not less than 178 and the oil shall conform to all the other requirements as above.

2. SAMPLING

The method of sampling given under (*a*) below should be used whenever it is feasible to apply it. To meet conditions when (*a*) is not applicable, method (*b*), (*c*), or (*d*) is to be used, according to the special conditions that obtain.

(*a*) During Loading of Tank Cars or Filling of Containers for Shipment at the Factory.—The purchaser's inspector shall draw a sample at the discharge pipe where it enters the receiving vessel or vessels. The total sample shall be not less than 5 gallons and shall be a composite of small samples of not more than 1 pint each taken at regular intervals during the entire period of loading or filling.

The sample thus obtained shall be thoroughly mixed, and from this composite sample three portions of not less than 1 quart each shall be placed in clean dry glass bottles or tin cans which must be filled with the sample and securely stoppered with new clean corks or well-fitting metal covers or caps. These shall be sealed and labeled distinctly by the inspector, and one delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(*b*) From Loaded Tank Cars or other Large Vessels.—The total sample shall be not less than 5 gallons and shall be a composite of numerous small samples of not more than 1 pint each taken from the top, bottom, and intermediate points by means of a glass or metal container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths when the stopper or top is removed and the container allowed to fill. The sample thus obtained is handled as in (*a*).

(*c*) Barrels and Drums.—Not less than 5 per cent of the packages in any shipment or delivery of barrels and drums shall be sampled. The packages shall be shaken, rolled, and stirred to thoroughly mix the contents. The samples from the individual containers shall be taken through the bung hole or holes not less than 1¼ inch in diameter bored in the head or side for the purpose. The apparatus for drawing the sample shall consist of a glass tube about 1 inch in diameter and somewhat longer than the length or diameter of the oil container, a conical stopper that will fit the glass tube and is not more than ½ inch long fastened to a stiff metal rod not more than ¼ inch in diameter and not less than 4 inches longer than the glass tube. The stopper is lowered by

the rod until it rests on the bottom of the cask, the tube slipped down slowly over the rod, and finally pressed on the stopper. By holding tube and rod the column of oil can then be removed. This process is repeated until the required amount of sample is obtained, which must be not less than 2 gallons. This is mixed and handled as in (*a*)

(*d*) Small Containers, Cans, etc., of 10 Gallons or Less.—Small containers, cans, etc., of 10 gallons or less should be sampled while filling by method (*a*) whenever possible. When method (*a*) is not applicable, it is mutually agreed that: In all cases the total sample taken shall not be less than 3 quarts. This shall be obtained by taking at least one package from each lot of not more than 300 packages. The sample thus taken shall be thoroughly mixed and subdivided as in (*a*).

3. LABORATORY EXAMINATION

Samples shall, in general, be tested by the following methods, but the purchaser reserves the right to apply any additional tests such as specific tests for foreign oils, rosin, etc., or use any available information to ascertain whether the material meets the specification. The laboratory sample shall be thoroughly mixed by shaking, stirring, or pouring from one vessel to another and the samples for the individual tests taken from this thoroughly mixed sample.

(*a*) Loss on Heating at 105 to 110° C.—Place 10 g of the oil in an accurately weighed 200 cc Erlenmeyer flask; weigh. Heat in an oven at a temperature between 105 and 110° C for 30 minutes; cool and weigh. Calculate the percentage loss. This determination shall be made in a current of dry carbon dioxide gas.

(*b*) Foots.—With all materials at a temperature between 20 and 27° C mix, by shaking in a stoppered flask for exactly one minute, 25 cc of the well-shaken sample of oil, 25 cc of acetone (see 4(*a*)) and 10 cc of the acid calcium chloride solution (see 4(*b*)). Transfer the mixture to a burette where settling can take place for 24 hours. The temperature during this period should be between 20 and 27° C.

The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read in tenths of a cubic centimeter or a fraction thereof. This reading multiplied by four expresses the amount of foots present as percentage by volume of the oil taken.

(*c*) Specific Gravity.—Use a pyknometer accurately standardized and having a capacity of at least 25 cc or any other equally accurate method, making the test at 15.5° C, water being unity at 15.5° C.

(*d*) Acid Number.—Weigh from 5 to 10 g of the oil. Transfer to a 350 cc Erlenmeyer flask. Add 50 cc of neutral 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask. Heat on a steam bath for 30 minutes. Cool and add phenolphthalein indicator. Titrate to a faint permanent pink color with the standard sodium hydroxide solution. Calculate the acid number (milligrams KOH per gram of oil).

(*e*) Saponification Number.—Weigh about 2 g of the oil in a 350 cc Erlenmeyer flask. Add 25 cc alcoholic sodium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on the steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with half normal sulphuric acid. Run two blanks with the alcoholic sodium hydroxide solution. (See 4(*h*).) These should check within 0.1 cc N/2 H_2SO_4. From the difference between the number of cubic centimeters of N/2 H_2SO_4 required for the blank and for the determination, calculate the saponification number (milligrams KOH required for 1 g of oil).

(*f*) Unsaponifiable Matter.—Weigh 8 to 10 g of the oil. Transfer to a 250 cc, long-neck flask. Add 5 cc of strong solution of sodium hydroxide (equal weights of NaOH and H_2O), and 50 cc 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agitate the flask to break up the liquid but do not project the liquid onto the sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 cc.

Transfer to a 500 cc glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc, add 100 cc redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500 cc separatory funnel and repeat the process using 60 cc of ether. After thorough separation draw off the aqueous solution into a 400 cc beaker, then the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 cc of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel.

Shake the combined ether solution with the accumulated water rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two portions of water (about 25 cc each). Add these to the main water solution.

Swirl the separatory funnel so as to bring the last drops of water down to the stopcock, and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise if necessary) into a 250 cc flask and distill off. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool and weigh. (*The unsaponifiable oil from adulterated drying oils is volatile and will evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of ether is gone.*)

(*g*) IODINE NUMBER.—Place a small quantity of the sample in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see 4 (*g*)) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titration and the titration on the samples and the iodine value of the thiosulphate solution, calculate the iodine number of the samples tested. (Iodine number is centigrams of iodine to 1 g of sample.)

(*h*) ASH.—Tare a porcelain crucible or dish. Add 10 to 25 cc of oil, carefully weighing the amount added. Place on a stone slab on the floor of a hood. Ignite by playing the flame of a burner on the surface of the oil and allow to burn quietly until most of the oil is burned off; then transfer to a muffle or over a flame and continue heating at a very low temperature (not over a dull red) until all carbonaceous matter is consumed. Cool,

weigh, and calculate the percentage of ash. Moisten the ash with a few drops of water and test with litmus paper. Record whether neutral or alkaline. Wash any ash adhering to the test paper back into the crucible. Dissolve the ash in dilute nitric acid to which a little hydrogen peroxide has been added. After solution is complete make up the volume to about 50 cc with nitric acid and water so that the final volume will contain about 1 volume of concentrated nitric acid and 3 volumes of water. Boil to remove excess of hydrogen peroxide. Determine manganese by the bismuthate method as described in Treadwell-Hall, Analytical Chemistry, third edition, volume 2, page 617.

Ash another portion of the oil and dissolve the ash as above in nitric acid and hydrogen peroxide. Transfer to a 250 cc beaker and dilute to about 200 cc. This volume of solution should contain 15 to 20 cc of concentrated nitric acid. Electrolyze this solution using platinum electrodes (the anode being previously weighed) with a current density of about 0.5 ampere and 2 to 2.5 volts. It is best to pass the current overnight (about 15 hours). On removing the anode, it is carefully washed in clear water, dried in a steam oven, transferred to an oven where it is heated to 180° C, cooled and weighed. The increase in weight of the anode multiplied by 0.86 gives the weight of lead in the sample. Calculate to percentage. If desired, the lead may be determined by the sulphate or any other accurate method in place of the electrolytic method given above.

(*i*) Time of Drying on Glass.—Flow the oil over a perfectly clean glass plate and allow to drain in a vertical position in a well-ventilated room at a temperature between 15 and 39° C. After about 2 hours the film is tested at intervals with the finger at points not less than 2½ cm from the edges. The film will be considered dry when it adheres no longer to the finger and does not rub up appreciably when the finger is rubbed lightly across the surface. With boiled linseed oil this usually occurs in from 5 to 18 hours.

(*j*) Color.—Prepare a fresh solution of pure potassium bichromate in pure strong (1.84 specific gravity) colorless sulphuric acid. For raw oil, this solution should be in the proportion of 1.0 g potassium bichromate to 100 cc (184.0 g) sulphuric acid. For refined oil, the solution should be in the proportion of 0.1 g potassium bichromate to 100 cc sulphuric acid. Place the oil and colored solution in separate thin-walled, clear glass tubes of

the same diameter (1 to 2 cm) to a depth of not less than 2.5 cm and compare the depths of color by looking transversely through the columns of liquid by transmitted light.

4. REAGENTS FOR TESTING

The following reagents will be required:

(*a*) Acetone that will pass the specification of the United States Pharmacopoeia.

(*b*) Acid Calcium Chloride Solution.—Saturate with calcium chloride a mixture of 90 parts water and 10 parts concentrated hydrochloric acid (specific gravity 1.2).

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide in the proportion so that 24.83 g crystallized sodium thiosulphate will be present in 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Analytical Chemistry, Treadwell-Hall, Vol. II, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved. Dilute to 1 liter.

(*e*) Standard Iodine Solution.—Dissolve 13 g of resublimed iodine and 18 g of pure potassium iodide (free from iodates) in 50 cc of distilled water, and dilute to 1000 cc. Determine its exact value by titrating with the standard sodium thiosulphate solution.

(*f*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

(*g*) Hanus Solution.—Dissolve 13.2 g of iodine in 1000 cc of glacial acetic acid (99.5 per cent) that will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*h*) Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving sodium hydroxide in water in the proportion of 200 g NaOH to 200 cc water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. Determine the exact strength by titrating against pure benzoic acid (C_6H_5COOH) using phenolphthalein as indicator. (See Bureau of Standards Scientific Paper 183.) This solution will be approximately one-fourth normal, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it.

(*i*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

(*j*) Half Normal Sulphuric Acid Solution.—Add about 15 cc sulphuric acid (1.84 specific gravity) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly half normal strength or leave as originally made, applying appropriate correction.

5. BASIS OF PURCHASE

Material is to be purchased by weight or volume as specified in the contract. When purchased by weight, the price shall be quoted per pound or per hundred pounds. When purchased by volume, a gallon of oil shall mean 231 cubic inches, at 15.5° C.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

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UNITED STATES GOVERNMENT SPECIFICATION FOR BASIC CARBONATE WHITE LEAD, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 5.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

Basic carbonate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(*a*) DRY PIGMENT.—The pigment shall be the product made from metallic lead and shall have a composition corresponding approximately to the formula $2PbCO_3.Pb(OH)_2$. It shall be thoroughly washed after corroding, shall be free from impurities and adulterants, and shall meet the following requirements:

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Color—Color strength.—When specified, shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum.	Maximum.
	Per cent.	Per cent.
Coarse particles retained on Standard No. 325 screen		1.0
Lead carbonate	65.0	75.0
Total impurities, including moisture		2.0

(*b*) PASTE.—The paste shall be made by thoroughly grinding the above-described pigment with pure raw or refined linseed oil. The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Minimum.	Maximum.
	Per cent.	Per cent.
Pigment	90	92
Linseed oil	8	10
Moisture and other volatile matter		0.7
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)		1.5

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test. When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

Whenever possible, an original unopened container shall be sent to the laboratory with the paste; and when this is for any reason not done, the inspector shall determine by testing thoroughly with a paddle or spatula whether the material meets the requirement regarding not caking in the container. (See 4 (*a*).) After assuring himself that the paste is not caked, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

3. LABORATORY EXAMINATION OF DRY PIGMENT.

(*a*) Color.—Take 1 g of the sample, add 10 to 12 drops linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 1 g of the standard basic carbonate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white or whiter than the "standard," it passes this test. If the standard is whiter than the sample, the material does not meet the specification.

(*b*) Color Strength.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 5 drops of linseed oil, and rub up with a flat-bottomed glass pestle, or muller, then add exactly 10 g of the sample and 45 drops of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edge spatula and grind out two more times in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner, except that 10 g of standard basic carbonate white lead is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light or lighter in color than the standard, it passes this test. If the standard is lighter in color than the sample, the material does not meet the specification.

(*c*) Coarse Particles.[1]—Dry in an oven at 105° to 110° C. a No. 325 screen, cool and weigh accurately. Weight 25 g of the sample; dry at 100° C.; transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, was all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool and weigh.

(*d*) Qualitative Analysis.—Test for matter insoluble in acetic acid, zinc, calcium, etc., by the regular methods of qualitative analysis.

(*e*) Moisture.—Place 1 g of the sample in a tared wide-mouth short weighing tube provided with a glass stopper. Heat with

[1] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the United States.

stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool and weigh. Calculate loss in weight as moisture.

(*f*) TOTAL LEAD AND INSOLUBLE IMPURITY.—Weigh 1 g of the sample, moisten with water, dissolve in acetic acid. If any insoluble residue remains, filter, dry at 105 to 110° C. and weigh as insoluble impurity. Dilute the solution to about 200 cc, make alkaline with NH_4OH, then acid with acetic acid, heat to boiling and add 10 to 15 cc of a 10 per cent solution of sodium bichromate or potassium bichromate, and heat until the yellow precipitate assumes an orange color. Let it settle and filter on a Gooch crucible, washing by decantation with hot water until the washings are colorless, and finally transferring all the precipitate. Then wash with 95 per cent ethyl alcohol and then with ethyl ether; dry at 100° C. and weigh $PbCrO_4$. Calculate to lead oxide ($PbCrO_4 \times 0.69 = PbO$). Total lead may be determined by the sulphate method if preferred.

(*g*) CARBON DIOXIDE.—Determine by evolution with dilute acid and absorption in soda-lime or KOH solution, calculate CO_2 to $PbCO_3$, subtract PbO equivalent from total PbO and calculate residual PbO to $Pb(OH)_2$.

$$CO_2 \times 6.072 = PbCO_3$$
$$CO_2 \times 5.072 = PbO$$
$$PbO \times 1.197 = PbCO_3$$
$$PbO \times 1.08 = Pb(OH)_2$$

4. LABORATORY EXAMINATION OF PASTE.

(*a*) CAKING IN CONTAINER.—When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of white-lead paste. The paste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, 30 cc linseed oil added slowly with

careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*c*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish, about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(*d*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, add enough of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of the extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C., or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment.

(*e*) Examination of Pigment.—Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube and apply tests 3(*a*), 3(*b*), 3(*d*), 3(*f*), and 3(*g*).

(*f*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole add 15 cc of aqueous sodium hydroxide (see reagents) and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water; then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask, add 25 to 50 g of anhydrous sodium sulphate.

Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat at a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*g*) TEST FOR MINERAL OIL.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water and mix. A clear solution indicates absence of more than a trace of unsaponifiable matter. If the solution is not clear, the oil is not pure linseed oil.

(*h*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let it stand with occasional shakings for one-half hour. Add 10 cc of the 15 per cent potassium-iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titration on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample, and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If

the iodine number is less than 170, the oil does not meet the specification.

(*i*) Coarse Particles and "Skins."—Weigh an amount of paste containing 25 g of pigment (see 4 (*d*)), add 100 cc kerosene, wash through a No. 325 screen and weigh the residue as in 3 (*c*).

5. REAGENTS.

(*a*) Extraction Mixture—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine.[2] This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, boil the mixture until the starch is practically dissolved, and then dilute to one liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g iodine in 1,000 cc of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine, about 3 cc to double the halogen content, which is determined by titration. The iodine may be dissolved by applying heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium-Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of

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[2] See Treadwell-Hall Analytical Chemistry, II, 3d ed., p. 646.

about 22 g per 1,000 cc. Let the solution stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

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UNITED STATES GOVERNMENT SPECIFICATION FOR BASIC SULPHATE WHITE LEAD, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 6.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

Basic sulphate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(*a*) Dry Pigment.—The pigment shall be the sublimed product prepared from lead sulphide ores, free from impurities and adulterants, and shall meet the following requirements:

Color—Color Strength.—When specified shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum.	Maximum.
Coarse particles:	Per cent.	Per cent.
Retained on standard No. 325 screen		1.0
Composition:		
Lead oxide	11.0	18.0
Zinc oxide		9.0
Total impurities, including moisture		1.0
The remainder shall be lead sulphate.		

(*b*) PASTES.—The paste shall be made by thoroughly grinding the dry pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. It shall mix readily in all proportions without curdling with linseed oil, turpentine, or volatile mineral spirits or any combination of these substances.

The paste shall consist of:

	Minimum.	Maximum.
	Per cent.	Per cent.
Pigment	89	91.0
Linseed oil	9	11.0
Moisture and other volatile matter		0.7
Coarse particles and "skins" (total residue retained on No. 325 screen, based on pigment)		1.5

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4*a*.) After assuring himself that the paste is not caked in the container the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION OF DRY PIGMENT.

(*a*) COLOR.—Take 1 g of the sample, add 10 to 12 drops linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in

a similar manner, 1 g of the standard basic sulphate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white as or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(*b*) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 5 drops of linseed oil and rub up with a flat-bottomed glass pestle or muller, then add exactly 10 g of the sample and 45 drops of linseed oil and grind with a circular motion of the muller 50 times; gather up with a sharp-edge spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner except that 10 g of standard basic sulphate white lead is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(*c*) COARSE PARTICLES.[1]—Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh 25 g of the sample, dry at 100° C.; transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

(*d*) QUALITATIVE ANALYSIS.—Test for matter insoluble in acid ammonium acetate solution, for calcium, for carbonates, and for any other impurities suspected by the regular methods of qualitative analysis.

(*e*) MOISTURE.—Place 1 g of the sample in a tared, wide mouth, short weighing tube provided with a glass stopper. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

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[1] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the educational bureau, scientific section, Paint Manufacturers' Association of the United States.

(*f*) Insoluble Impurity and Total Lead.—In a 250 cc beaker, moisten 1 g of the pigment with a few drops of alcohol; add 50 cc of acid ammonium acetate solution. (See Reagents 5*a*.) Heat to boiling and boil for 2 minutes. Decant through a filter paper, leaving any undecomposed matter in the beaker. To the residue in the beaker, add 50 cc of the acid ammonium acetate solution, heat to boiling, and boil for 2 minutes. Filter through the same paper and wash with hot water. If an appreciable residue remains, ignite and weigh as insoluble impurity. Unite the acid ammonium acetate solutions, heat to boiling, and add dropwise, with stirring, a slight excess (in total about 10 to 15 cc) of dichromate solution. (See Reagents 5*b*.) Heat until the precipitate assumes an orange color, let settle, filter on a weighed Gooch crucible, wash by decantation with hot water until the washings are colorless, and finally transfer all of the precipitate to the crucible. Then wash with 10 cc of 95 per cent ethyl alcohol and finally with 10 cc of ethyl ether. Dry at 110 to 120° C., cool, and weigh $PbCrO_4$. Calculate to PbO by multiplying by the factor 0.69.

(*g*) Zinc Oxide.—Weigh accurately about 1 g of the pigment, transfer to a 400 cc beaker, add 30 cc of HCl (1:2), boil for 2 or 3 minutes, add 200 cc of water and a small piece of litmus paper, add NH_4OH until slightly alkaline, render just acid with HCl, then add 3 cc of concentrated HCl, heat nearly to boiling, and titrate with standard potassium ferrocyanide as in standardizing that solution. (See Reagents 5*d*.) Calculate total zinc as ZnO.

(*h*) Lead Sulphate.—Treat 0.5 g of the pigment in a 400 cc beaker with a few drops of alcohol, add 10 cc of bromine water, 10 cc of HCl (1:1), and 3 g of NH_4Cl. Cover with a watch glass and heat on a steam bath for 5 minutes, add hot water to give a total volume of about 200 cc, boil for 5 minutes, filter to separate any insoluble matter (a pure pigment should be completely dissolved), and wash thoroughly with hot water. (The insoluble matter may be ignited, weighed, and examined qualitatively.) Neutralize the clear solution (original solution or filtrate from insoluble matter) in a covered beaker with dry Na_2CO_3, add 1 g more of dry Na_2CO_3, and boil 10 to 15 minutes. Wash off cover, let settle, filter, and wash with hot water. Redissolve the precipitate in HCl (1:1), reprecipitate with Na_2CO_3 as above, filter, and wash thoroughly with hot water. Acidify the united filtrates with HCl, adding about 1 cc in excess. Boil to expel bromine,

and to the clear boiling solution add slowly with stirring 15 cc of barium chloride solution. (See Reagents 5*e*.) Let stand on steam bath for about one hour, filter on a weighed Gooch crucible, wash thoroughly with boiling water, dry, ignite, cool, and weigh as $BaSO_4$. Calculate to $PbSO_4$, using the factor 1.3.

(*i*) CALCULATIONS.—Calculate the percentage of $PbSO_4$ to PbO by multiplying by the factor 0.736 and subtract the result from the percentage of PbO found under (*f*); report the difference as PbO. Report ZnO found under (*g*) as percentage of ZnO. Moisture and insoluble matter are reported as such.[2]

4. LABORATORY EXAMINATION OF PASTE.

(*a*) CAKING IN CONTAINER.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of white lead paste. The paste shall be finally thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out from it.

(*b*) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, and 30 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*c*) MOISTURE AND OTHER VOLATILE MATTER.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish, about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(*d*) PERCENTAGE OF PIGMENT.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water,

[2] A method given by Schaeffer, J., Ind. and Eng. Chem., 6, p. 200 (1914), based on calculation of composition after determination of moisture, impurities, total lead, and total zinc oxide, is sometimes used. This method requires very accurate determination of Pb and ZnO, since the errors of determination are multiplied by approximately four in making the calculation to PbO and Pbso4.

and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment.

(*e*) Examination of Pigment.—Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube, and examine as under 3 (*a*), 3(*b*), 3(*d*), 3 (*f*), 3(*g*), 3(*h*), and 3 (*i*), Laboratory Examination of Dry Pigment.

(*f*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole add 15 cc of aqueous sodium hydroxide (see Reagents), and 75 cc of ethyl alcohol, mix, and heat uncovered on a steam bath until saponification is complete (about 1 hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and $PbSO_4$ precipitate, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask, add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.[3]

[3] It is important to follow all of the details since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(*g*) Test for Mineral Oil.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for 5 minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear the oil is not pure linseed oil.

(*h*) Iodine Number of Fatty Acids.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker and weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform and whirl the bottle to dissolve the sample. Add 10 cc of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents 5*k*) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titration on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*i*) Coarse Particles and "Skins."—Weigh out an amount of paste containing 25 g of pigment (see *d*), add 100 cc of kerosene, wash through No. 325 screen, and weigh the residue as in 3 (*c*).

5. REAGENTS.

(*a*) Acid Ammonium Acetate Solution.—Mix 150 cc of 80 per cent acetic acid, 100 cc of water, and 95 cc of strong ammonium (specific gravity 0.90).

(*b*) Dichromate Solution.—Dissolve 100 g sodium dichromate ($Na_2Cr_2O_7 2H_2O$) or potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1,000 cc.

(*c*) Uranyl Indicator for Zinc Titration.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*d*) Standard Potassium Ferrocyanide.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize,

transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure ZnO to a 400 cc beaker. Dissolve in 10 cc of HCl and 20 cc of water. Drop in a small piece of litmus paper, add NH_4OH until slightly alkaline, then add HCl until just acid and finally add 3 cc of strong HCl. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing 1 minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume and acidity as obtain when the sample is titrated.

(*e*) Barium Chloride Solution.—Dissolve 100 g of pure crystallized barium chloride in water and dilute to 1,000 cc.

(*f*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from CO_2 in the proportion of 24.83 g of crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*g*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, and boil the mixture until the starch is practically dissolved; then dilute to 1 liter.

(*h*) Extraction Mixture.—Mix 10 volumes ether (ethyl ether), 6 volumes benzol, 4 volumes methyl alcohol, and 1 volume acetone.

(*i*) Aqueous Sodium Hydroxide.—Dissolve 100 g of NaOH in distilled water and dilute to 300 cc.

(*j*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(*k*) Hanus Solution.—Dissolve 13.2 g of iodine in 1,000 cc of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine to double the halogen content, de-

termined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*l*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g to 1,000 cc) kept at about 50° C. for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 87.

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UNITED STATES GOVERNMENT SPECIFICATION FOR ZINC OXIDE, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION No. 8.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

Zinc oxide may be ordered in the form of dry pigment or paste ground in linseed oil. Purchases shall be made on the basis of net weight.

The pigment may be American process zinc oxide, made direct from the ore, or French process zinc oxide, made from spelter. The contract shall state which kind is desired.

The color and color strength when specified shall be equal to samples mutually agreed upon by buyer and seller.

109842°—22

The pigment shall meet the following requirements:

	Maximum.	Minimum.
	Per cent.	Per cent.
Coarse particles retained on Standard No. 325 screen	1.0	....

	American process.		French process.	
	Maximum.	Minimum.	Maximum.	Minimum.
	Per cent.	Per cent.	Per cent.	Per cent.
Zinc oxide	....	98	....	99
Total sulphur	0.2	....	0.1	....
Total impurities, including moisture	2.0	....	1.0	....

The paste shall be made by thoroughly grinding the above pigment with pure raw or refined linseed oil. The paste shall not cake in the container and shall break up readily in oil to form a smooth paint of brushing consistency.

The paste shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	86	82
Linseed oil	18	14
Coarse particles and "skins" (total residue left on No. 325 screen based on pigment)	1.5	....
Moisture and other volatile matter	0.5	....

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole.

With the dry pigment, this package is to be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test. When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done, the inspector shall determine by thoroughly testing with a paddle or spatula whether the material meets the requirement regarding not caking in the container. (See 4 (*a*).) After assuring himself that the paste is not caked in the can, the

inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean, dry metal or glass container which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

3. LABORATORY EXAMINATION OF DRY PIGMENT.

(*a*) COLOR.—Take 5 g of the sample, add 1.5 cc of linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 5 g of the standard zinc oxide. Spread the two pastes side by side on a clear colorless glass plate and compare the colors. If the sample is as white as or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(*b*) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 0.2 cc of linseed oil and rub up with a flat-bottomed glass pestle or muller, than add exactly 10 g of the sample and 2.5 cc of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner except that 10 g of standard zinc oxide is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(*c*) COARSE PARTICLES.[1]—Dry in an oven at 105 to 110° C. a 325 screen, cool and weigh accurately. Weigh 10 g of the sample; dry at 100° C., transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool and weigh.

[1] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the United States.

(*d*) Qualitative Analysis.—Test for matter insoluble in hydrochloric acid, for lead, calcium, etc., by regular methods of qualitative analysis.

(*e*) Zinc Oxide.—With samples free from impurities (see (*d*)), ignite a weighed sample and calculate the residue as ZnO. With samples containing impurity, proceed as follows: Weigh accurately about 0.25 g, transfer to a 400 cc beaker, moisten with alcohol, dissolve in 10 cc of hydrochloric acid and 20 cc of water and titrate with standard potassium ferrocyanide following the procedure used in standardizing this reagent. (See 5(*i*).)

(*f*) Total Sulphur.—Weigh accurately about 10 g of the sample. Moisten with a few drops of alcohol, add 5 cc of bromine water (saturated solution of bromine), then concentrated hydrochloric acid in excess, boil to expel bromine, and dilute to about 100 cc. (Material complying with the specification should all go into solution; if insoluble matter remains, filter and examine by appropriate methods.) Make alkaline with ammonia, then just acid with hydrochloric acid, heat to boiling and add about 10 cc of hot barium chloride solution. (See Reagents.) Let stand several hours (overnight), filter on a weighed Gooch crucible, wash thoroughly with hot water, dry, ignite, cool, and weigh the $BaSO_4$. Calculate to S ($BaSO_4$ x $0.1373 = S$).

4. LABORATORY EXAMINATION OF PASTE.

(*a*) Caking in Container.—When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of zinc oxide paste. The paste shall be finally thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 35 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*c*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish, about 5 cm in diameter, spreading the paste over the bottom.

Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage moisture and other volatile matter.

(*d*) PER CENT PIGMENT.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc portions of extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for 2 hours. Cool, weigh, and calculate percentage of pigment.

(*e*) EXAMINATION OF PIGMENT.—Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube and apply tests 3 (*d*), (*e*), and (*f*). If required, apply tests 3 (*a*) and (*b*) in comparison with a portion of pigment extracted from the standard paste in exactly the same manner as in extracting the sample.

(*f*) PREPARATION OF FATTY ACIDS.—To about 25 g of the paste in a porcelain casserole add 15 cc aqueous sodium hydroxide (see Reagents), and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water; then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask, and add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear

above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the either is entirely driven off.

NOTE.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*g*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for 5 minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*h*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand, with occasional shaking, for one-half hour. Add 10 cc of the 15 per cent potassium-iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*i*) COARSE PARTICLES AND "SKINS."—Weigh an amount of paste containing 10 g of pigment (see 4 (*d*)), add kerosene, and wash through a No. 325 screen as in 3 (*c*). The residue is reported as "Coarse particles and skins."

5. REAGENTS.

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Analytical Chemistry, Treadwell-Hall, vol. 11, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days and then distilled.

(*h*) Uranyl Indicator for Zinc Titration.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*i*) Standard Potassium Ferrocyanide.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc beaker. Dissolve in 10 cc hydrochloric acid and 20 cc water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then add 3 cc strong hydrochloric acid. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

(*j*) Barium Chloride Solution.—Dissolve 100 g of pure crystallized barium chloride in water and dilute to 1,000 cc.

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BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 88.

[2d edition. Issued July 3, 1922.]

UNITED STATES GOVERNMENT SPECIFICATION FOR LEADED ZINC OXIDE, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 9.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

Leaded zinc oxide, frequently known as leaded zinc, consists of zinc oxide and varying amounts of lead compounds. It may be ordered in the form of dry pigment or paste ground in linseed oil. Purchases shall be made on the basis of net weight.

The pigment may be high-leaded zinc oxide or low-leaded zinc oxide. The contract shall state which kind is desired. The color and color strength when specified shall be equal to samples mutually agreed upon by buyer and seller.

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The pigment shall meet the following requirements:

	Maximum.	Minimum.
	Per cent.	Per cent.
Coarse particles retained on Standard No. 325 screen	1.0	

	High-leaded.		Low-leaded.	
	Maximum.	Minimum.	Maximum.	Minimum.
	Per cent.	Per cent.	Per cent.	Per cent.
Zinc oxide (ZnO)		60		93
Water soluble salts	1.0		1.0	
Total impurities, including moisture	1.5		1.5	

The balance to be normal or basic lead sulphate.

The paste shall be made by thoroughly grinding the above pigment with pure raw or refined linseed oil. The paste shall not cake in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	88.0	
Linseed oil		12.0
Moisture and other volatile matter	0.5	
Coarse particles and "skins" (total residue left on No. 325 screen based on pigment)	1.5 ~~15~~	

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole.

With the dry pigment, the package is to be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4 (*a*.) After assuring himself that the paste is not caked in the container, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with

a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION OF DRY PIGMENT.

(*a*) COLOR.—Take 5 g of the sample, add 1.5 cc of linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 5 g of the standard leaded zinc oxide. Spread the two pastes side by side on a clear colorless glass plate and compare the colors. If the sample is as white or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(*b*) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 0.2 cc of linseed oil, and rub up with a flat-bottomed glass pestle or muller; then add exactly 10 g of the sample and 2.5 cc of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner, except that 10 g of standard leaded zinc oxide is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(*c*). COARSE PARTICLES.[1]—Dry in an oven at 105° to 110° C. a 325 screen, cool and weigh accurately. Weigh 10 g of the sample; dry at 100° C., transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105° to 110° C., cool and weigh.

[1] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the U. S.

(*d*) Qualitative Analysis.—Test for matter insoluble in hydrochloric acid, lead, calcium, carbon dioxide, etc., by regular methods of qualitative analysis.

(*e*) Moisture.—Place 1 g of the sample in a wide-mouth short weighing tube provided with a glass stopper. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

(*f*) Water Soluble Salts.—To 10 g of pigment in a 500 cc volumetric flask, add 200 cc of water, boil for five minutes, nearly fill the flask with hot water, allow to cool, fill to mark, mix, filter through a dry paper, discard the first 50 cc of filtrate, transfer 100 cc of the filtrate (corresponding to 2 g of sample) to a weighed dish, evaporate to dryness, heat for one hour in an oven at 105 to 110° C., cool, and weigh, calculate to percentage of water soluble salts.

(*g*) Zinc Oxide.—Weigh accurately about 0.3 g of the pigment, transfer to a 400 cc beaker, add 30 cc of hydrochloric acid (1 : 2), boil for two or three minutes, add 200 cc of water and a small piece of litmus paper; add ammonium hydroxide until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc of strong hydrochloric acid, heat nearly to boiling, and titrate with standard potassium ferrocyanide as in standardizing the solution. (See Reagents 5 (*d*).) Calculate total zinc as ZnO.

(*h*) Calculations.—If, as will be the case with material complying with the specification, no metals but zinc and lead are found by qualitative tests, add the percentage of ZnO, moisture, and water soluble salts and subtract the sum from 100. Call the remainder "normal and basic lead sulphate."

4. LABORATORY EXAMINATION OF PASTE.

(*a*) Caking in Container.—When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of leaded-zinc oxide paste. The paste shall be finally thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 35 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle, the resulting mixture must be smooth and of good brushing consistency.

(*c*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and other volatile matter.

(*d*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate percentage of pigment.

(*e*) Examination of Pigment.—Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube, and apply tests 3 (*d*), (*f*), (*g*), and (*h*). If required, apply tests 3 (*a*) and (*b*) in comparison with a portion of pigment extracted from the standard paste in exactly the same manner as in extracting the sample.

(*f*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see Reagents) and 75 cc of ethyl alcohol; mix, and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice); boil, stir, and transfer to a separatory funnel, to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the

aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off completely the water layer. Transfer the ether solution to a dry flask, add 25 to 50 g. of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary, through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*g*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for five minutes, add 40 cc of water and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*h*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the

sample and the iodine value of the thiosulphate solution calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*i*) COARSE PARTICLES AND "SKINS."—Weigh an amount of paste containing 10 g of pigment (see 4(*d*)), add 100 g of kerosene and wash through a No. 325 screen. The residue is reported as "coarse particles and 'skins.'"

5. REAGENTS.

(*a*) URANYL INDICATOR FOR ZINC TITRATION.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*b*) STANDARD POTASSIUM FERROCYANIDE.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc beaker. Dissolve in 10 cc of hydrochloric acid and 20 cc of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid and then add 3 cc of strong hydrochloric acid. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run, using the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

(*c*) BARIUM CHLORIDE SOLUTION.—Dissolve 100 g of pure crystallized barium chloride in water and dilute to 1,000 cc.

(*d*) STANDARD SODIUM THIOSULPHATE SOLUTION.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g of crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine (See Analytical Chemistry, Treadwell-Hall, 2, 3d ed., p. 646). This solution will be approximately decinormal, and it is best to leave it as

it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*e*) STARCH SOLUTION.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*f*) EXTRACTION MIXTURE.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*g*) AQUEOUS SODIUM HYDROXIDE.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*h*) POTASSIUM IODIDE SOLUTION.—Dissolve 150 g of potassium iodide free from iodate, in distilled water and dilute to 1,000 cc

(*i*) HANUS SOLUTION.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*j*) ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle, and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 89.

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UNITED STATES GOVERNMENT SPECIFICATION FOR WHITE PAINT AND TINTED PAINTS MADE ON A WHITE BASE, SEMIPASTE AND READY MIXED.[1]

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 10.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

White paint and tinted paints made on a white base may be ordered either in the form of semipaste pigment ground in linseed oil or of ready-mixed paint.

The semipaste shall be purchased by net weight, the ready-mixed paint either by weight or volume (231 cubic inches to the gallon).

(*a*) PIGMENT.—The pigment shall be composed of:

	Maximum.	Minimum.
	Per cent.	Per cent.
White lead (basic carbonate, basic sulphate, or a mixture thereof)	70	45
Zinc oxide (ZnO)	55	30
White mineral pigments, containing no lead or zinc compounds, pure tinting colors, or any mixture thereof	15	0

[1] It is believed that this specification admits practically all high-grade prepared paints generally available in the United States, and which are therefore obtainable without requiring manufacturers to make up special lots. On large contracts for which paint will be specially made, the purchaser may require the bidder to submit the formula of the paint he proposes to furnish as conforming to the specifications.

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In no case shall the sum of the basic lead carbonate, basic lead sulphate, and zinc oxide be less than 85 per cent. The lead and zinc pigments may be introduced in the form of any mixture preferred of basic carbonate white lead, basic sulphate white lead, zinc oxide, or leaded zinc, provided the above requirements as to composition are met. The total lead dissolved by dilute acetic acid and hot acid ammonium acetate, weighed as lead sulphate, and this weight multiplied by the factor 0.883 shall be considered white lead. (It is not possible to determine the amount of lead carbonate and lead sulphate when carbonates or sulphates of other metals such as calcium are present. Also neither basic lead carbonate nor basic lead sulphate are definite compounds. The factor to convert $PbSO_4$ to $(PbCO_3)_2\ Pb(OH)_2$ is 0.854, to convert $PbSO_4$ to $PbSO_4PbO$ is 0.868, and to convert $PbSO_4$ to $(PbSO_4)_2\ PbO$ is 0.913. The arbitrary factor used under this specification is the mean of the largest and smallest of these three factors.

(*b*) LIQUID.—The liquid in semipaste paint shall be entirely pure raw or refined linseed oil; in ready-mixed paint it shall contain not less than 90 per cent pure raw linseed oil, the balance to be combined drier and thinner. The thinner shall be turpentine, volatile mineral spirits, or a mixture thereof.

(*c*) SEMIPASTE.—Semipaste shall be made by thoroughly grinding the pigment with pure raw or refined linseed oil.

The semipaste as received and three months thereafter shall be not caked in the container and shall break up readily in linseed oil to form a smooth paint of brushing consistency. It shall mix readily with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances, in all proportions without curdling. The color and hiding power when specified shall be equal to that of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 19.0 pounds. The paste shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	77	73
Linseed oil	27	23
Moisture and other volatile matter	0.7	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	2.0	....

(*d*) READY-MIXED PAINT.—Ready-mixed paints shall be well ground, shall not settle badly or cake in the container, shall be readily broken up with a paddle to a smooth uniform paint of good

brushing consistency, and shall dry within 18 hours to a full oil gloss, without streaking, running, or sagging. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 15¾ pounds. The paint shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	66	62
Liquid (containing at least 90 per cent linseed oil)	38	34
Water	0.5	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	2.0	....

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine by thorough testing with a paddle or spatula whether the material meets the requirement regarding caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds of the thoroughly mixed paint, place it in a clean, dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with tne inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION—SEMIPASTE.

(*a*) CAKING IN CONTAINER.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up than a normal good grade of semipaste paint. The semipaste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed

semipaste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Color.—Place some of the paint on a clean, clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(*c*) Weight per Gallon.—From the weight of a known volume of the paste calculate the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom about 75 mm high and having a capacity of from 125 to 175 cc (a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is determined to within 1 cc. The paste is packed into it until completely full, the top leveled off smooth with a spatula, and weighed to ± 0.5 g. Subtract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within ± 2 in the second decimal place.

(*d*) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 18 cc linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*e*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(*f*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours.

Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and preserve in a stoppered bottle.

(*g*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see reagents) and 75 cc of ethyl alcohol mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

Note.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*h*) Test for Mineral Oil and Other Unsaponifiable Matter.—Place 10 drops of the fatty acid (*g*) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

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(*i*) Iodine Number of Fatty Acids.—Place a small quantity of the fatty acids (*g*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) into a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*j*) Coarse Particles and Skins.—Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh an amount of semipaste containing 10 g of pigment (see 3 (*f*)), add 100 cc of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

4. ANALYSIS OF PIGMENT.

(*a*) Qualitative Analysis.—A complete qualitative analysis following the well-established methods is always advisable, but the work may be usually very much shortened by adding acetic acid slowly to the pigment until all carbonate is decomposed (noting whether any hydrogen sulphide is evolved), then adding a large excess of acid ammonium acetate, boiling, filtering, and testing the filtrate for metals other than lead and zinc (especially calcium and barium). The absence of calcium in this filtrate indicates that the extending pigments contain no calcium carbonate or calcium sulphate; the absence of barium indicates that the extending pigments contain no barium carbonate. Test another portion

of pigment with hydrochloric acid (1:1). No odor of hydrogen sulphide should develop.

(*b*) White Lead.—Weigh accurately about 1 g of the pigment, transfer to a 250 cc beaker, moisten with a few drops of alcohol, add slowly dilute (about 20 per cent) acetic acid until all carbonate is decomposed (no further effervescence), then add 50 cc of acid ammonium acetate solution (see reagents), and boil for two minutes. Decant through a weighed Gooch crucible, leaving any undecomposed matter in the beaker. Wash the Gooch crucible with a small amount (about 20 cc) of hot water. To the residue in the beaker add 50 cc of the acid ammonium acetate solution and boil two minutes. Filter through the same Gooch crucible, transferring the insoluble matter to the crucible, and wash thoroughly with hot water. Dry the crucible at 105 to 120° C., cool, and weigh. In cases where siliceous material was used as the white extending pigments, the material retained on the Gooch crucible will approximate the amount of white extending and tinting pigments.

Unite the filtrates and pass in a stream of hydrogen sulphide to complete precipitation; let the mixed sulphides of lead and zinc settle, filter on paper, wash with water containing hydrogen sulphide, dissolve the sulphides in hot nitric acid (1:3), and determine lead as sulphate in the usual manner, weighing as $PbSO_4$. Multiply lead sulphate weight by the factor 0.883 and report as white lead.

(*c*) Zinc Oxide.—Weigh accurately about 1 g of the pigment, transfer to a 400 cc beaker, add 30 cc of hydrochloric acid (1:2), boil for two or three minutes, add 200 cc of water and a small piece of litmus paper; add strong ammonia until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc of strong hydrochloric acid, heat nearly to boiling, and titrate with standard ferrocyanide as in standardizing that solution (see reagents). Calculate total zinc as zinc oxide.

(*d*) *Calculations.*—Add the percentage of white lead (see 4(*b*)), zinc oxide (see 4(*c*)), and subtract from 100; the remainder is reported as extending and tinting pigments.

5. LABORATORY EXAMINATION—MIXED PAINT.

(*a*) Caking in Container.—Follow the procedure outlined in 3(*a*), noting that the paint should be no more difficult to break up than a good grade of mixed paint.

(*b*) Color.—Follow the procedure outlined in 3(*b*).

(*c*) Weight per Gallon.—Weigh a clean, dry, 100 cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(*d*) Brushing Properties and Time of Drying.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let stand for 18 hours. The paint should be dry and free from streaks.

(*e*) Water.—Mix 100 g of the paint in a 300 cc flask with 75 cc of toluol. Connect with a condenser and distill until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint.

(*f*) Volatile Thinner.—Follow the procedure outlined in 3(*e*). Correct the result for any water found (see 5(*e*)) and report the remainder as volatile thinner.

(*g*) Percentage of Pigment.—Follow the procedure outlined in 3(*f*).

(*h*) Testing Nonvolatile Vehicle.—Follow the procedure outlined in 3(*g*), 3(*h*), and 3(*i*), except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam bath until all volatile thinner is driven off.

(*i*) Coarse Particles and Skins.—Follow the procedure outlined in 3(*j*).

(*j*) Testing Pigment.—Follow the procedure outlined in 4(*a*) to 4(*d*), inclusive.

6. REAGENTS.

(*a*) Acid Ammonium Acetate Solution.—Mix 150 cc of 80 per cent acetic acid, 100 cc of water, and 95 cc of strong ammonia (specific gravity, 0.90).

(*b*) Uranyl Indicator for Zinc Titration.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*c*) Standard Potassium Ferrocyanide.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize,

transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc beaker. Dissolve in 10 cc of hydrochloric acid and 20 cc of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then 3 cc of strong hydrochloric acid. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtained when the sample is titrated.

(*d*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*e*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*f*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*g*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*h*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1,000 cc

(*i*) Hanus Solution.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*j*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

No. 90

[2d edition. Issued May 23, 1922]

UNITED STATES GOVERNMENT SPECIFICATION FOR RED LEAD—DRY AND PASTE

FEDERAL SPECIFICATIONS BOARD

STANDARD SPECIFICATION NO. 11

This Specification was officially adopted by the Federal Specifications Board, on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS

1. GENERAL

Red lead may be ordered in the form of dry pigment or of paste ground in pure raw linseed oil. Two grades of pigment, known as 85 and 95 per cent, may be ordered, and each contract shall state which grade is desired.[1]

Material shall be bought by net weight.

[1] Avoid storing red-lead paste in places of high temperature, as heat accelerates the tendency of this material to cake or harden. Purchasers are cautioned not to buy red lead in paste form unless it is to be used within three months after shipment by the contractor.

98004°—22

(*a*) Dry Pigment.—The pigment shall consist entirely of oxides of lead free from all adulterants and shall meet the following requirements:

	85 per cent grade	95 per cent grade
	Per cent	Per cent
True red lead (Pb_3O_4), not less than	85	95
Total impurities, including moisture, soluble matter, water— and matter insoluble in a mixture of nitric acid and hydrogen peroxide, not more than	1	1
Remainder shall be lead monoxide (PbO).		
Coarse particles: Retained on standard No. 325 screen, not more than	2.0	1.0

When mixed with raw linseed oil, turpentine, and liquid drier in the proportions

Dry red lead	pounds	20
Raw linseed oil	pints	5
Turpentine	gills	2
Liquid drier	do	2

the resulting paint when brushed on a smooth vertical iron surface shall dry hard and elastic without running, streaking, or sagging.

(*b*) Paste.—The paste shall be made by thoroughly grinding the specified grade of dry pigment with pure raw or refined linseed oil.

The paste, as shipped by the contractor, and for three months thereafter, shall not be caked in the container and shall readily break up in oil to form a smooth paint of brushing consistency. The paste shall have the following composition:

	Maximum	Minimum
	Per cent	Per cent
Pigment	94	92
Linseed oil	8	6
Moisture and other volatile matter	0.5	....
Coarse particles and skins (total residue left on No. 325 screen)	1.5	....

When mixed with raw linseed oil, turpentine, and liquid drier in the proportions

Red lead paste	pounds	20
Raw linseed oil	pints	4½
Turpentine	gills	2
Liquid drier	do	2

the resulting paint when brushed on a smooth vertical iron surface shall dry hard and elastic without running, streaking, or sagging.

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole.

With the dry pigment, this package is to be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test. When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine by thoroughly testing with a paddle or spatula whether the material meets the requirement regarding not caking in the container (see 4 (*a*)). After assuring himself that the paste is not caked in the can, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

Samples will, in general, be tested by the following methods, but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specification.

3. LABORATORY EXAMINATION, DRY PIGMENT

(*a*) Qualitative Analysis.—Follow ordinary methods of qualitative analysis. The material should give a negative test for matter insoluble in a mixture of nitric acid and hydrogen peroxide, and material other than oxides of lead. (If more than a faint cloud remains after treatment with nitric acid and hydrogen peroxide, it will be necessary to take a weighed sample and determine the percentage of this insoluble matter.) Boil 2 g of the sample with 25 cc of 95 per cent ethyl alcohol, let settle, decant off the supernatant liquid, boil the residue with water, decant as before, and boil the residue with very dilute ammonia. If the

alcohol, water, or ammonia are colored, organic coloring matter is indicated, which is cause for rejection.

(*b*) True Red Lead.—Weigh accurately 1 g of the sample into a 200 cc Erlenmeyer flask, add a few drops of distilled water, and rub the mixture to a smooth paste with a glass rod flattened on the end. Mix in a small beaker 30 g of pure crystallized sodium acetate, 2.4 g of pure potassium iodide, 10 cc of water, and 10 cc of 50 per cent acetic acid. Stir until all is liquid, warm gently, and, if necessary, add 2 to 3 cc more water. Cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved, add 30 cc of water containing 5 to 6 g of sodium acetate, and titrate at once with standard sodium thiosulphate solution, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off the rod, and add the sodium thiosulphate solution until pale yellow. Add starch solution and titrate until colorless, add standard iodine solution until the blue color is just restored. From the amount of standard iodine solution used, calculate the correction to be applied to the thiosulphate reading, and calculate true red lead (iodine value of thiosulphate $\times 2.7 = Pb_3O_4$ value).

(*c*) Water Soluble Matter.—Digest 10 g of the sample with 200 cc of hot water on a steam bath for 1 hour; filter and wash with hot water until no residue is left on evaporating a few drops of the washings. Evaporate the filtrate to dryness in a weighed dish on a steam bath, heat for 30 minutes at 105 to 110° C, cool, and weigh.

(*d*) Coarse Particles.—Dry in an oven at 105 to 110° C a 325 screen, cool, and weigh accurately. Weigh 25 g of the sample, dry at 100° C, transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C, cool, and weigh.[2]

[2] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the United States.

(*e*) Running, Streaking, or Sagging.—Mix paint and apply as per specifications. About the smallest amount that can be conveniently made up will be 154 g dry red lead, 40 cc raw linseed oil, and 4 cc each of turpentine and liquid drier.

4. LABORATORY EXAMINATION, PASTE

(*a*) Caking in Container.—When an original package is received in the laboratory, it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of red-lead paste. The paste shall finally be thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Mixing with Linseed Oil, Running, Streaking, and Sagging.—Mix as per specification to a paint, first using only the linseed oil and noting whether the paste breaks up readily and the resulting mixture is smooth. About the smallest amount that can be conveniently made up will be 154 g red-lead paste, 36 cc raw linseed oil, and 4 cc each of turpentine and liquid drier.

(*c*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish, about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C for one hour, cool, and weigh. Calculate the loss in weight as percentage of moisture and other volatile matter.

(*d*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C or on top of a warm oven for 10 minutes,

then in an oven at 110 to 115° C for 2 hours. Cool, weigh, and calculate percentage of pigment.

(*e*) Examination of Pigment.—Grind the pigment from (*d*) to a fine powder, pass through a No. 80 screen to remove any "skins," preserve in a stoppered tube, and apply tests 3 (*a*), 3 (*b*), and 3 (*c*).

(*f*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see reagents), and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and lead sulphate precipitate, wash once with water; then add 50 cc water and 50 cc ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask, add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (Pass through $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

Note.—It is important to follow all of the details, since ether generally contains alcohol, and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(*g*) Test for Mineral Oil.—Place 10 drops of the fatty acid (*f*) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable

matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*h*) Iodine Number of Fatty Acids.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*i*) Coarse Particles and Skins.—Weigh an amount of paste containing 25 g of pigment (see 4 (*d*)), add 200 cc of kerosene, and wash through a No. 325 screen as in 3 (*d*).

5. REAGENTS

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g of crystallized sodium thiosulphate to 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 11, 3d ed., p. 646.) This solution will be approximately decinormal and it is best to

leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with solda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Standard Iodine Solution.—Dissolve 13 g of resublimed iodine and 18 g of pure potassium iodide (free from iodates) in 50 cc of distilled water, and dilute to 1000 cc. Determine its exact value by titrating with the standard sodium thiosulphate solution.

(*f*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide, free from iodate, in distilled water and dilute to 1000 cc.

(*g*) Hanus Solution.—Dissolve 13.2 g of iodine in 1000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*h*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

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UNITED STATES GOVERNMENT SPECIFICATION FOR OCHER, DRY AND PASTE

FEDERAL SPECIFICATIONS BOARD

STANDARD SPECIFICATION NO. 12

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS

1. GENERAL

Ocher may be required in the form of dry pigment or paste ground in linseed oil; it shall be prepared in accordance with the most improved methods. Grinding in oil shall be thorough and the vehicle shall be pure raw linseed oil.

The material shall be bought by net weight.

(*a*) Dry Pigment.—The pigment shall be a hydrated oxide of iron permeating a siliceous base, and shall be free from added impurities. It shall conform to the following requirements:

Color—Color Strength—Tone.—Equal to sample mutually agreed on by buyer and seller.

	Maximum	Minimum
	Per cent	Per cent
Coarse particles: Retained on standard No. 325 screen	3.0	
Iron oxide		17
Lime (CaO)	5	
Lead chromate	None	
Organic colors	None	

(*b*) PASTE.—Ocher in paste form shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment	71	69
Linseed oil	31	29
Moisture and volatile matter	0.5	
Coarse particles and "skins" (total residue left on No. 325 screen) based on pigment	3.5	

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages shall be taken as representative of the whole.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4 (*a*).) He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds. This sample shall be placed in a clean, dry, metal or glass container which it must nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION OF DRY PIGMENT

(*a*) COLOR AND TONE.—Weigh 1 g each of the color and standard and rub up separately on a glass plate or stone slab, using the same amount of bleached linseed oil in each case. Place portions of each side by side on a clean strip of glass, turn the glass over and compare the colors. Rubbing up (mixing with oil) is best done with a muller, and should be such that no lumps remain and that the consistency of both paste portions is the same.

Smear (with the finger) portions of the pastes on a clear glass strip and compare the tone by transmitted light.

(*b*) COLOR STRENGTH.—Weigh accurately 0.05 g each of the color and standard and two portions of 1 g each of the zinc oxide. Add the color to one of the portions of zinc oxide and the standard to the other and rub up separately in linseed oil until on spreading out no dark streaks are visible. Place the color and standard tints side by side on a clean glass strip, turn the strip over and compare.

(*c*) COARSE PARTICLES.[1]—Dry in an oven at 105 to 110° C a 325 screen, cool and weigh accurately. Weigh 10 g of the sample; dry at 100° C, transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps; wash with kerosene through the screen, breaking up all lumps but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C, cool and weigh.

(*d*) MOISTURE.—Place 1 g of the sample in a wide-mouth, short weighing tube provided with a glass stopper, and weigh accurately. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool and weigh. Calculate loss in weight as moisture.

(*e*) ORGANIC COLORING MATTER (A. S. T. M. "Standards," 1918, p. 656).—Test the pigment successively with hot water, 95 per cent alcohol, alcoholic sodium hydroxide and acetic acid. Chloroform, sodium hydroxide, sulphuric acid, hydrochloric acid-stannous chloride solution, and other reagents may be tried. The solutions should remain colorless. The presence of an organic color may often be detected by the characteristic odor given off on ignition.

(*f*) TOTAL IRON OXIDE.—Ignite 1 g of the sample in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 500 cc Erlenmeyer flask and add 20 cc of 1 : 1 hydrochloric acid. Digest just short of boiling until no dark specks can be seen in the insoluble residue. When the residue is light in color, the solution of iron may be considered complete. Dilute to 100 cc and without filtering, add 3 g of granulated zinc; put a funnel in the neck of the flask and heat when the action slackens; if basic iron salts separate out, add a few drops of hydrochloric acid. When the

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[1] For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the U. S.

reduction is complete, add 30 cc of sulphuric acid (1 : 2) and as soon as the residual zinc is dissolved, wash down the funnel and neck of the flask with a fine jet of water. Now add 200 cc of cool water and 30 cc of titrating solution (see reagents) and titrate with standard potassium permanganate. Run a blank on the zinc and calculate ferric oxide (Fe_2O_3). Any other accurate method for determining iron may be used at the option of the analyst.

(*g*) Test for Lead and Calcium by the Usual Qualitative Methods.—If calcium is present in appreciable amount, determine it as follows: Ignite 2.5 g in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 500 cc graduated flask; add 100 cc of 1 : 1 hydrochloric acid. Digest just short of boiling until no dark specks can be seen in the insoluble residue; add ammonia in slight excess and about 2 cc of hydrogen peroxide solution; cool, dilute to 500 cc; mix thoroughly, filter through a dry paper. Take 100 cc of the filtrate (corresponding to 0.5 g of sample), heat to boiling, add a few drops of ammonia and an excess of a hot saturated ammonium oxalate solution. Continue boiling until the precipitate becomes granular; let stand about 30 minutes, filter, wash with hot water until free from ammonium oxalate. Pierce the apex of the filter with a stirring rod and wash the precipitate into the beaker with hot water; pour warm dilute sulphuric acid (1 : 4) through the paper and wash a few times. Add about 30 cc of sulphuric acid (1 : 4), dilute to about 250 cc with hot water and titrate at once with standard potassium permanganate solution (the solution should not be below 60° C when the end point is reached). Calculate to CaO. (The Fe value of $KMnO_4 \times 0.502 =$ CaO value.)

4. LABORATORY EXAMINATION OF PASTE

(*a*) Caking in Container.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of ocher paste. The paste shall be finally thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and portions for the remaining tests promptly weighed out from it.

(*b*) Mixing with Oil, or Thinning.—Add sufficient linseed oil to 100 g of the sample to make a liquid paint of proper consistency for application with a brush, noting the amount of oil necessary. Note the smoothness with which the paint works under the brush.

(*c*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(*d*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C for two hours. Cool, weigh, and calculate the percentage of pigment.

(*e*) Examination of the Pigment.—Grind the pigment from (*d*) to a fine powder, pass through an 80-mesh screen to remove any skins, preserve in a stoppered bottle, and examine as under 3(*e*), 3(*f*), and 3(*g*).

(*f*) Color, Tone, and Color Strength.—Extract the pigment from the vehicle with extraction mixture as in 4(*d*), except that it is not necessary to accurately weigh the amount taken, and after washing with ether, dry in a vacuum at a temperature not above 70° C. Grind this extracted pigment fine enough to pass a No. 80 screen to remove skins, and test as under 3(*a*) and 3(*b*).

(*g*) Coarse Particles and Skins.—Weigh an amount of paste containing 10 g of pigment (see 4(*d*)), add 200 cc of kerosene, and wash through a No. 325 screen as in 3(*c*).

(*h*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see reagents) and 75 cc of ethyl alcohol, mix and heat uncovered

on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and insoluble mineral matter, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary, through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

NOTE. It is important to follow all of the details, since ether generally contains alcohol and, after washing with water, always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(*i*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acids (*h*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for 5 minutes, add 40 cc of water and mix; a clear solution indicates than not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*j*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of fatty acids (*h*) in a small weighing burette or beaker. Weigh accurately. Transfer, by dropping, about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine amount of sample

used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand, with occasional shaking, for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample, and the iodine value of the thiosulphate solution calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

5. REAGENTS

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulpate Solution. — Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g crystallized sodium thiosulphate to 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g of iodine in 1000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic

acid. Add enough bromine to double the halogen content, determine by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

(*h*) Potassium Permanganate Solution.—Dissolve 5.7 g of pure potassium permanganate in a liter of distilled water, let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize as follows: In a 400 cc beaker dissolve 0.40 to 0.50 g of Bureau of Standards' sodium oxalate in 250 cc of hot water (80 to 90° C) and add 15 cc of dilute sulphuric acid (1:1). Titrate at once with the potassium permanganate solution, *stirring the liquid vigorously and continuously.* The permanganate must not be added more rapidly than 10 to 15 cc per minute, and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution should not be below 60° C by the time the end point is reached. (Too rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as a stirring rod is most convenient.) The weight of sodium oxalate used multiplied by 0.8334 gives its iron equivalent. The permanganate solution should be kept in a glass stoppered bottle painted black to keep out light.

(*i*) Titrating Solution.—Dissolve 160 g of manganese sulphate in water, dilute to 1750 cc, add 330 cc of orthophosphoric acid (specific gravity 1.72), and 320 cc of concentrated sulphuric acid.

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BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

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UNITED STATES GOVERNMENT SPECIFICATION FOR IRON-OXIDE AND IRON-HYDROXIDE PAINTS

FEDERAL SPECIFICATIONS BOARD

STANDARD SPECIFICATION No. 13

This Specification was officially adopted by the Federal Specifications Board, on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

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1. GENERAL

This specification applies to iron-oxide and iron-hydroxide paints of red and brown colors. The paint may be ordered in the form of either semipaste paint or ready-mixed paint.

The basis of purchase may be either by net weight or by volume (231 cubic inches to the gallon).

(*a*) PIGMENT.—The pigment in both semipaste and ready-mixed paint shall be very finely ground iron oxide, iron hydroxide, siliceous minerals or a mixture thereof, to which carbon pigment may be added, if necessary, to produce the required color. It must be free from organic coloring matter (dyes or lakes). The pigment shall show on analysis not less than 30 per cent of ferric

oxide (Fe_2O_3). The total of the ferric oxide, insoluble siliceous matter, and loss on ignition shall be not less than 90 per cent.

(*b*) LIQUID.—The liquid in semipaste paint shall be entirely pure raw or refined linseed oil; in ready-mixed paint it shall contain not less than 75 per cent pure raw linseed oil, the balance to be combined drier and thinner. The thinner shall be turpentine, volatile mineral spirits, or a mixture thereof.

(*c*) SEMIPASTE.—Semipaste shall be made by thoroughly grinding the pigment with pure raw or refined linseed oil.

The semipaste as received and three months thereafter shall be not caked in the container and shall break up readily in linseed oil to form a smooth paint of brushing consistency. It shall mix readily with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances, in all proportions without curdling. The color and hiding power when specified shall be equal to that of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 13½ pounds. The paste shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment	72.0	68.0
Linseed oil	32.0	28.0
Moisture and other volatile matter	.7	
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	3.5	

(*d*) READY-MIXED PAINT.—Ready-mixed paints shall be well ground, shall not settle badly or cake in the container, shall be readily broken up with a paddle to a smooth uniform paint of good brushing consistency, and shall dry within 18 hours to a full oil gloss, without streaking, running, or sagging. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. The weight per gallon shall not be less than 12 pounds. The paint shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment	57.0	53.0
Liquid (containing at least 75 per cent linseed oil)	47.0	43.0
Water	.5	
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	3.5	

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages shall be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine by thorough testing with a paddle or spatula whether the material meets the requirement regarding caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds of the thoroughly mixed paint, place it in a clean, dry metal or glass container, which it shall nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION—SEMIPASTE

(*a*) Caking in Container.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up than a normal good grade of semipaste paint. The semipaste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed semipaste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Color.—Place some of the paint on a clean, clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(*c*) Weight per Gallon.—From the weight of a known volume of the paste calculate the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom about 75 mm high and having a capacity of from 125 to 175 cc (a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is determined to within 1 cc. The paste is packed into it until completely full, the top leveled off smooth with a spatula, and weighed to ± 0.5 g. Sub-

tract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within ± 2 in the second decimal place.

(*d*) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 30 cc linseed oil added slowly, with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*e*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tarred flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(*f*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and preserve in a stoppered bottle.

(*g*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see Reagents) and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw of the aqueous layer and wash the

ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary, through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C on a dry hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*h*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*g*) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*i*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*g*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) into a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the

titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodone number is less than 170, the oil does not meet the specification.

(*j*) Coarse Particles and Skins.—Dry in an oven at 105 to 110° C a No. 325 screen, cool, and weigh accurately. Weigh an amount of semipaste containing 10 g of pigment (see 3 (*f*)), add 50 cc of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C, cool, and weigh.

4. ANALYSIS OF PIGMENT

(*a*) Organic Coloring Matter.—(A. S. T. M. Standards, 1918, p. 656). Test the pigment successively with hot water, 95 per cent alcohol, alcoholic sodium hydroxide, and acetic acid. Chloroform, sodium hydroxide, sulphuric acid, hydrochloric acid-stannous chloride solution, and other reagents may be tried. The solutions should remain colorless. The presence of an organic color may often be detected by the characteristic odor given off on ignition.

(*b*) Total Iron Oxide.—Ignite 1 g of the pigment in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 500 cc Erlenmeyer flask and add 20 cc of 1 : 1 hydrochloric acid. Digest just short of boiling till no dark specks can be seen in the insoluble residue. When the residue is light in color, the solution of iron may be considered complete. Dilute to 100 cc and without filtering, add 3 g of granulated zinc; put a funnel in the neck of the flask and heat when the action slackens; if basic iron salts separate out, add a few drops of hydrochloric acid. When the reduction is complete, add 30 cc of sulphuric acid (1 : 2), and as soon as the residual zinc is dissolved, wash down the funnel and neck of the flask with a fine jet of water. Now add 200 cc of cool water and 30 cc of titrating solution (see reagents) and titrate with standard potassium permanganate. Run a blank on the zinc and calculate iron as Fe_2O_3. Any other accurate method for determining iron may be used at the option of the analyst.

(*c*) Loss on Ignition.—Ignite 1 g of the pigment to constant weight. It is safest to use a porcelain crucible for this purpose.

(*d*) Insoluble Siliceous Matter.—Transfer 1 g of the pigment to a porcelain dish, ignite at a dull red heat to destroy organic matter, cool, add 20 cc of hydrochloric acid, 1 : 1, cover and heat on a steam bath until no dark specks can be seen in the insoluble residue. Remove cover, add 10 cc of strong hydrochloric acid, evaporate to dryness on a steam bath, moisten with hydrochloric acid, add water, and wash on to a filter paper with hot water; wash, ignite, and weigh the insoluble siliceous matter.

5. LABORATORY EXAMINATION—MIXED PAINT

(*a*) Caking in Container.—Follow the procedure outlined in 3(*a*), noting that the paint should be no more difficult to break up than a good grade of mixed paint.

(*b*) Color.—Follow the procedure outlined in 3(*b*).

(*c*) Weight per Gallon.—Weigh a clean, dry, 100 cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(*d*) Brushing Properties and Time of Drying.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let stand for 18 hours. The paint shall be dry, smooth, and free from streaks.

(*e*) Water.—Mix 100 g of the paint in a 300 cc flask with 75 cc of toluol. Connect with a condenser and distill until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint. Material complying with the specification should yield less than 0.5 cc.

(*f*) Volatile Thinner.—Follow the procedure outlined in 3(*e*). Correct the result for any water found (see 5(*e*)) and report the remainder as volatile thinner.

(*g*) Percentage of Pigment.—Follow the procedure outlined in 3(*f*).

(*h*) Testing Nonvolatile Vehicle.—Follow the procedure outlined in 3(*g*), 3(*h*), and 3(*i*), except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam bath until all volatile thinner is driven off.

(*i*) Coarse Particles and Skins.—Follow the procedure outlined in 3(*j*).

(*j*) Testing Pigment.—Follow the procedure outlined in 4(*a*) to 4(*d*), inclusive.

6. REAGENTS

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g of crystallized sodium thiosulphate to 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g of iodine in 1000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used,

and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

(*h*) Potassium Permanganate Solution.—Dissolve 5.7 g of pure potassium permanganate in a liter of distilled water, let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize as follows: In a 400 cc beaker dissolve 0.40–0.50 g of Bureau of Standards' sodium oxalate in 250 cc of hot water (80 to 90° C) and add 15 cc of dilute sulphuric acid (1 : 1). Titrate at once with the potassium permanganate solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10 to 15 cc per minute, and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution should not be below 60° C by the time the end point is reached. (More rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as a stirring rod is most convenient.) The weight of sodium oxalate used multiplied by 0.8334 gives its iron equivalent. The permanganate solution should be kept in a glass-stoppered bottle painted black to keep out light.

(*i*) Titrating Solution.—Dissolve 160 g of manganese sulphate in water, dilute to 1750 cc, add 330 cc of orthophosphoric acid (specific gravity 1.72), and 320 cc of concentrated sulphuric acid.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 94.

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UNITED STATES GOVERNMENT SPECIFICATION FOR BLACK PAINT, SEMIPASTE AND READY MIXED.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 14.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

Black paint may be ordered in the form of either semipaste paint or ready-mixed paint.

The basis of purchase may be either by net weight or by volume (231 cubic inches to the gallon).

(*a*) PIGMENT.—The pigment in both semipaste and ready-mixed paints shall consist of carbon, lead oxide, insoluble mineral material, and, at the option of the manufacturer, oxide of iron. The pigment shall show on analysis not less than 20 per cent of carbon and not less than 5 per cent of lead oxide calculated as

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Pb_3O_4. The total of the lead oxide, iron oxide, insoluble siliceous material, and loss on ignition shall be not less than 90 per cent.

(*b*) LIQUID.—The liquid in semipaste paint shall be entirely pure raw or refined linseed oil; in ready-mixed paint it shall contain not less than 80 per cent pure raw linseed oil, the balance to be combined drier and thinner. The thinner shall be turpentine, volatile mineral spirits, or a mixture thereof.

(*c*) SEMIPASTE.—Semipaste shall be made by thoroughly grinding the pigment with pure raw or refined linseed oil.

The semipaste as received and three months thereafter shall be not caked in the container and shall break up readily in linseed oil to form a smooth paint of brushing consistency. It shall mix readily with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances, in all proportions without curdling. The color and hiding power when specified shall be equal to that of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 10 pounds. The paste shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	52	48
Linseed oil	52	48
Moisture and other volatile matter	0.7	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	1.5	....

(*d*) READY-MIXED PAINT.—Ready-mixed paint shall be well ground, shall not settle badly or cake in the container, shall be readily broken up with a paddle to a smooth uniform paint of good brushing consistency, and shall dry within 18 hours to a full oil gloss, without streaking, running, or sagging. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 9 pounds. The paint shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	32	28
Liquid (containing at least 80 per cent linseed oil)	72	68
Water	0.5	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	1.5	....

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine by thorough testing with a paddle or spatula whether the material meets the requirements regarding caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds of the thoroughly mixed paint, place it in a clean, dry metal or glass container, which it shall nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION—SEMIPASTE.

(*a*) Caking in Container.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up than a normal good grade of semipaste paint. The semipaste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed semipaste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) Color.—Place some of the paint on a clean clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(*c*) Weight per Gallon.—From the weight of a known volume of the paste calculate the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom about 75 mm. high and having a capacity of from 125 to 175 cc (a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is deternined to within 1 cc. The paste is packed into it until completely full, the top

leveled off smooth with a spatula, and weighed to ±0.5 g. Subtract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within ±2 in the second decimal place.

(*d*) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 70 cc linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(*e*) Moisture and Other Volatile Matter.—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(*f*) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and preserve in a stoppered bottle.

(*g*) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see reagents) and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form

an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary, through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*h*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*g*) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*i*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*g*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) into a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the

difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*j*) COARSE PARTICLES AND SKINS.—Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh an amount of semipaste containing 10 g of pigment (see 3 (*f*)), add 50 cc of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

4. ANALYSIS OF PIGMENT.

(*a*) QUALITATIVE ANALYSIS.—Make qualitative analysis following ordinary methods.

(*b*) LOSS ON IGNITION.—Ignite 1 g of the pigment in a weighed porcelain crucible until all carbon is consumed. It is best to use gentle heat with free access of air. Cool, weigh, and calculate the percentage of loss on ignition.

(*c*) CARBON AND INSOLUBLE MINERAL MATERIAL.—Place 1 g of the pigment in a porcelain dish, moisten with a few drops of alcohol, add 20 cc of concentrated hydrochloric acid, cover, and heat on steam bath for 15 minutes. Remove cover and evaporate to dryness, moisten with hydrochloric acid, add 25 cc of water, filter on a weighed Gooch crucible, and wash with hot water until the washings are free from lead and iron. Dry the crucible and contents at 105 to 110° C. for 2 hours. Ignite for 7 minutes in a current of dry carbon dioxide (using a Rose crucible cover) with a flame about 20 cm high. Cool in a current of dry carbon dioxide and weigh. Then ignite with free access of air (or in a current of oxygen) until all carbon is consumed. Cool and weigh. The loss in weight is calculated as carbon, and the residue remaining on the Gooch crucible is calculated as insoluble mineral material.

(*d*) LEAD OXIDE AND IRON OXIDE.—Determine lead and iron in the filtrate from the carbon determination by any convenient method, calculating lead to Pb_3O_4 and iron to Fe_2O_3.

5. LABORATORY EXAMINATION—MIXED PAINT.

(*a*) Caking in Container.—Follow the procedure outlined in 3(*a*), noting that the paint should be no more difficult to break up than a good grade of mixed paint.

(*b*) Color.—Follow the procedure outlined in 3(*b*).

(*c*) Weight per Gallon.—Weigh a clean, dry, 100 cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(*d*) Brushing Properties and Time of Drying.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let stand for 18 hours. The paint shall be dry, smooth, and free from streaks.

(*e*) Water.—Mix 100 g of the paint in a 300 cc flask with 75 cc of toluol. Connect with a condenser and distill until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint. Material complying with the specification should yield less than 0.5 cc.

(*f*) Volatile Thinner.—Follow the procedure outlined in 3(*e*). Correct the result for any water found (see 5(*e*)) and report the remainder as a volatile thinner.

(*g*) Percentage of Pigment.—Follow the procedure outlined in 3(*f*).

(*h*) Testing Nonvolatile Vehicle.—Follow the procedure outlined in 3(*g*), 3(*h*), and 3(*i*), except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam bath until all volatile thinner is driven off.

(*i*) Coarse Particles and Skins.—Follow the procedure outlined in 3(*j*).

(*j*) Testing Pigment.—Follow the procedure outlined in 4(*a*) to 4(*d*) inclusive.

6. REAGENTS.

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g of crystallized sodium thiosulphate to 1,000 cc. of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicyclic acid solution, add 300 to 400 cc. boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

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UNITED STATES GOVERNMENT SPECIFICATION FOR GREEN PAINT, SEMIPASTE AND READY MIXED.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 15.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

The paint contemplated by this specification is a chrome green paint, and it may be ordered either in the form of semipaste pigment ground in linseed oil or as ready-mixed paint.

The basis of purchase may be either net weight or volume (231 cubic inches to the gallon).

(*a*) PIGMENT.—The pigment in both semipaste and ready-mixed paints should be a chrome green containing about 23 per

cent of color (sum of lead chromate and insoluble Prussian blue), about 10 per cent of magnesium silicate, aluminum silicate, or similar siliceous material, and about 67 per cent of barium sulphate. It should be made by precipitating the color on the proper base rather than by mixing the individual materials. It must yield on analysis:

	Maximum.	Minimum.
	Per cent.	Per cent.
Color (total lead chromate and insoluble Prussian blue)		20
Material soluble in water, including soluble Prussian blue	0.2	
Acid-soluble or water-soluble calcium in any form, calculated as CaO	0.5	
Material other than color and barium sulphate	15	
The remainder must be barium sulphate.		

(*b*) Liquid.—The liquid in semipaste paint shall be entirely pure raw or refined linseed oil; in ready-mixed paint it shall contain not less than 90 per cent pure raw linseed oil, the balance to be combined drier and thinner. The thinner shall be turpentine, volatile mineral spirits, or a mixture thereof.

(*c*) Semipaste.—Semipaste paint shall be made by thoroughly grinding the pigment with pure raw or refined linseed oil.

The semipaste as received and three months thereafter shall be not caked in the container and shall break up readily in linseed oil to form a smooth paint of brushing consistency. It shall mix readily with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances, in all proportions, without curdling. The color and hiding power when specified shall be equal to that of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 16 pounds. The paste shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	72	68
Linseed oil	32	28
Moisture and other volatile matter	0.7	
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	2.5	

(*d*) Ready-Mixed Paint.—Ready-mixed paint shall be well ground, shall not settle badly or cake in the container, shall be readily broken up with a paddle to a smooth uniform paint of good brushing consistency, and shall dry within 18 hours to a full oil gloss, without streaking, running, or sagging. The color and hiding power when specified shall be equal to those of a sample

mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 12 pounds. The paint shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	55	50
Liquid (containing at least 90 per cent linseed oil)	50	45
Water	0.5	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	2.5	....

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages shall be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when this is for any reason not done, the inspector shall determine by thorough testing with a paddle or spatula whether the material meets the requirement regarding caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds. This sample shall be placed in a clean, dry metal or glass container, which it must nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION OF SEMIPASTE.

(*a*) CAKING IN CONTAINER. — When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up than a normal good grade of semipaste paint. The semipaste shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of thoroughly mixed semipaste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(*b*) COLOR.—Place some of the paint on a clean, clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(c) Weight per Gallon.—From the weight of a known volume of the paste calculate the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom about 75 mm high and having a capacity of from 125 to 175 cc (a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is determined to within 1 cc. The paste is packed into it until completely full, the top leveled off smooth with a spatula, and weighed to ± 0.5 g. Subtract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within ± 2 in the second decimal place.

(d) Mixing with Linseed Oil.—One hundred grams of the paste shall be placed in a cup, 30 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(e) Moisture and Other Volatile Matter. — Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(f) Percentage of Pigment.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and preserve in a stoppered bottle.

(g) Preparation of Fatty Acids.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium

hydroxide (see reagents) and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary, through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a $CaCl_2$ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry, hot plate until the ether is entirely driven off.

NOTE.—It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(*h*) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acids (*g*) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(*i*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*g*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) into a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine

test. Reweigh the burette or beaker and determine amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let stand with occasional shaking for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample and the iodine value of the thiosulphate solution, calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(*j*) Coarse Particles and Skins.—Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh an amount of semipaste containing 10 g of pigment (see 3 (*f*)), add 50 cc of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

4. ANALYSIS OF PIGMENT.

(*a*) Qualitative Analysis.—Test for Prussian blue by boiling a portion of the pigment with sodium hydroxide solution. A yellow or yellow-brown precipitate with a yellow liquid above it should result. Filter, add a mixture of ferric and ferrous salts to the filtrate, and render acid with dilute hydrochloric acid. A blue color indicates Prussian blue in the sample. Ignite another portion very gently to decompose the Prussian blue and make a qualitative analysis of the residue.

(*b*) Matter Soluble in Water.—Transfer 2.5 g of the pigment to a graduated 250 cc flask, add 100 cc of water, boil for 5 minutes, cool, fill to mark with water, mix, and allow to settle. Pour the supernatant liquid through a dry paper and discard the first 20 cc. Then evaporate 100 cc of the clear filtrate to dryness in a weighed dish, heat for one hour at 105 to 110° C., cool, and weigh.

(*c*) Barium Sulphate and Siliceous Material.—Heat a 1 g portion of the pigment very gently in a small porcelain dish. The heat must be so regulated by moving the burner that the Prussian blue is thoroughly decomposed without rendering the iron difficultly soluble. Allow to cool, transfer to a 400 cc beaker, add 20 cc of concentrated hydrochloric acid, heat on steam bath for 30 minutes, boil for 5 minutes, dilute with hot water to about 250 cc, filter on paper while hot, wash thoroughly with hot water until the washings are free from lead and chlorine, and ignite and weigh the residue, which will be barium sulphate and siliceous material. Mix the ignited residue with about 10 times its weight of anhydrous sodium carbonate (grinding the mixture in an agate mortar if necessary), and fuse the mixture in a covered platinum crucible, heating about one hour. Let cool, place crucible and cover in a 250 cc beaker, add about 100 cc of water, and heat until the melt is disintegrated. Filter on paper (leaving crucible and cover in beaker) and wash the beaker and filter thoroughly with hot water to remove soluble sulphates. Place the beaker containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the carbonate residue into the beaker by means of a jet of hot water. Wash the paper with hot, dilute hydrochloric acid (1:1), and then with hot water. If the carbonate residue is not completely dissolved, add sufficient dilute hydrochloric acid to effect solution, and remove crucible and cover, washing them with a jet of water. Heat the solution to boiling and add 10 to 15 cc of dilute sulphuric acid, and continue the boiling for 10 or 15 minutes longer. Let the precipitate settle, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as $BaSO_4$. Subtract from the result of the previous determination to obtain the siliceous material.

(*d*) Lead and Chromium.—Unite the filtrate and washings from barium sulphate and siliceous material (see (*c*)), dilute to 500 cc, nearly neutralize with ammonium hydroxide, and pass in a rapid stream of hydrogen sulphide until all the lead is precipitated as PbS; filter, wash with water containing a little hydrogen sulphide, dissolve in hot nitric acid (1:3), and determine lead as sulphate in usual manner, weighing as $PbSO_4$. Boil the filtrate from the lead sulphide to expel hydrogen sulphide. Add sodium peroxide in sufficient amount to render the solution alkaline and to oxidize the chromium to chromate. Boil until the hydrogen peroxide is driven off, cool, acidify with sulphuric acid

(1:4), add a measured excess of a freshly prepared solution of ferrous sulphate, and titrate the excess of ferrous iron with standard potassium dichromate, using potassium ferricyanide solution as outside indicator. Titrate a blank of an equal volume of the ferrous sulphate solution with the standard potassium dichromate. From the difference between the titration on the blank and on the sample, calculate the chromium in the sample to $PbCrO_4$. From the $PbCrO_4$ found, calculate the equivalent of $PbSO_4$ by multiplying by the factor 0.938. Subtract this value from the total $PbSO_4$ found above and report the remainder as lead compounds other than chromate, calculated as $PbSO_4$.

(*e*) Calcium.—Ignite 2 g of the pigment and dissolve the residue in hydrochloric acid as in 4(*c*). Then, without filtering from the insoluble matter, transfer to a 500 cc volumetric flask, saturate with hydrogen sulphide, make alkaline with ammonia, fill to the mark, mix, and filter through a dry paper, discarding the first 20 cc. Then determine the calcium in 250 cc of the filtrate (corresponding to 1 g pigment) by precipitation as oxalate and weighing as calcium oxide.

(*f*) Color.—Add the percentages of matter soluble in water 4(*b*), barium sulphate and siliceous material 4(*c*), lead compounds other than chromate calculated as $PbSO_4$ 4(*d*), and calcium oxide 4(*e*) and subtract the sum from 100. Call the difference the percentage of color.

5. LABORATORY EXAMINATION OF MIXED PAINT.

(*a*) Caking in Container.—Follow the procedure outlined in 3(*a*), noting that the paint should be no more difficult to break up than a good grade of mixed paint.

(*b*) Color.—Follow the procedure outlined in 3(*b*).

(*c*) Weight per Gallon.—Weigh a clean, dry, 100 cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(*d*) Brushing Properties and Time of Drying.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let stand for 18 hours. The paint should be dry and free from streaks.

(*e*) Water.—Mix 100 g of the paint in a 300 cc flask with 75 cc of toluol. Connect with a condenser and distill until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105° to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint.

(*f*) Volatile Thinner.—Follow the procedure outlined in 3(*e*). Correct the result for any water found (see 5(*e*)) and report the remainder as volatile thinner.

(*g*) Percentage of Pigment.—Follow the procedure outlined in 3(*f*).

(*h*) Testing Nonvolatile Vehicle.—Follow the procedure outlined in 3(*g*), 3(*h*), and 3(*i*), except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam bath until all volatile thinner is driven off.

(*i*) Coarse Particles and Skins.—Follow the procedure outlined in 3(*j*).

(*j*) Testing Pigment.—Follow the procedure outlined in 4(*a*) to 4(*e*), inclusive.

6. REAGENTS.

(*a*) Extraction Mixture.—

5 volumes benzol.
4 volumes methyl alcohol
1 volume acetone.

(*b*) Aqueous Sodium Hydroxide.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(*c*) Standard Sodium Thiosulphate Solution.—Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*d*) Starch Solution.—Stir up to 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solu-

tion, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(*e*) Potassium Iodide Solution.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(*f*) Hanus Solution.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(*g*) Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

(*h*) Standard Ferrous Sulphate Solution.—Dissolve 14 g of pure crystallized ferrous sulphate ($FeSO_4\ 7H_2O$) in about 500 cc of water, to which 25 cc of concentrated H_2SO_4 has been added, and then dilute to 1,000 cc. This solution should be freshly standardized when needed, as it does not keep well.

(*i*) Standard Potassium Dichromate Solution.—Dissolve 4.903 g of pure dry crystallized potassium dichromate in water and dilute to 1,000 cc. One cubic centimeter of this solution corresponds to 0.0108 g $PbCrO_4$, or 0.0101 g $PbSO_4$.

(*j*) Potassium Ferricyanide Solution.—Dissolve a piece half as big as a small pea in 50 cc of water. This solution must be made fresh when wanted, because it does not keep.

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BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

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UNITED STATES GOVERNMENT SPECIFICATION FOR WATER-RESISTING SPAR VARNISH.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION No. 18.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

The varnish shall be suitable for use on both outside and inside surfaces of vessels, buildings, etc., and must be resistant to air, light, and water. The manufacturer is given wide latitude in the selection of raw materials and processes of manufacture, so that he may produce a varnish of the highest quality. It must meet the following requirements:

APPEARANCE.—Clear and transparent.

COLOR.—Not darker than a solution of 3 g of potassium dichromate in 100 cc of pure sulphuric acid, specific gravity 1.84.

FLASH POINT (CLOSED-CUP).—Not below 30° C. (85° F.).

NONVOLATILE MATTER.—Not less than 40 per cent by weight.

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Set to Touch.—In not more than 5 hours.

Dry Hard and Tough.—In not more than 24 hours.

Working Properties.—Varnish must have good brushing, flowing, covering, and leveling properties.

Safety of Working.—Varnish must pass the draft test.

Water Resistance.—Dried film must withstand cold water for 18 hours and boiling water for 15 minutes without whitening or dulling.

Toughness.—Varnish must pass a 50 per cent Kauri reduction test at 24° C. (75° F.).

Note.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when for any reason this is not done the inspector shall thoroughly mix the contents of the container sampled, transfer not less than 1 quart to a clean dry glass bottle or tin can, which must be nearly filled with the sample, securely stoppered with a new clean cork or well-fitting cover or cap, sealed, and distinctly labeled by the inspector. The inspector should take a duplicate from the container sampled to be held for check in case of dispute, and, when requested, should take a sample for the seller.

3. LABORATORY EXAMINATION.

The tin panels used in the following tests shall all be cut from bright tin plate weighing not more than 25 g nor less than 19 g per square decimeter (0.51 to 0.39 pound per square foot). (Commercial No. 31 gage bright tin plate should weigh about 0.44 pound per square foot. It is important that the tin plate used shall be within the limits set.) The panels shall be about 7.5 by 13 cm (3 by 5 inches) and must be thoroughly cleaned with benzol immediately before using.

(*a*) Appearance.—Pour some of the thoroughly mixed sample into a clear glass bottle or test tube and examine by transmitted light. The varnish must be clear and transparent.

(*b*) Color.—Prepare a standard color solution by dissolving 3 g of pure powdered potassium dichromate in 100 cc of pure concentrated sulphuric acid of specific gravity 1.84. Gentle heat may be used if necessary to perfect the solution of the dichromate. The standard color solution and a sample of the varnish to be tested shall be placed in clear thin-walled glass tubes of the same diameter. The color comparison shall be made by placing the tubes close together and looking through them by transmitted light. The tubes used for this test should be 1.5 to 2.0 cm (⅝ to $\frac{13}{16}$ inch) in diameter and shall be filled to a depth of at least 2.5 cm (1 inch). (Since the potassium dichromate-sulphuric acid must be freshly made for this color comparison, it is frequently more convenient to compare samples with a permanently sealed tube of varnish which has previously been found to be slightly lighter in color than the standard solution of 3 g dichromate in sulphuric acid. When samples are found to be darker than this standard tube of varnish, the dichromate standard should be made up for final decision.)

(*c*) Flash Point.—Determine with either the Tag or Elliott closed-cup tester. The former is preferred.[1]

(*d*) Nonvolatile Matter.—Place a portion of the sample in a stoppered bottle or weighing pipette. Weigh container and sample. Transfer about 1.5 g of the sample to a weighed flat-bottomed metal dish about 8 cm in diameter (a friction-top can plug). Weigh container again and by difference calculate the exact weight of the portion of sample transferred to the weighed dish. Heat dish and contents in an oven maintained at 105 to 110° C. (221 to 230° F.) for three hours. Cool and weigh. From the weight of the residue left in the dish and weight of the sample taken calculate the percentage of nonvolatile residue.

(*e*) Drying Time.—Pour the varnish on one of the tin panels described above. Place the panel in a nearly vertical position in a well-ventilated room but not in the direct rays of the sun. The atmosphere of this room must be free from products of combustion or laboratory fumes. The temperature of the room should be from 21 to 32° C. (70 to 90° F.). The film is tested at points not less than 2.5 cm (1 inch) from the edges of the film by touching lightly with the finger. The varnish is considered to have set to touch when gentle pressure of the finger shows a tacky condition

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[1] Directions for using the Tag tester may be found in A. S. T. M. Standards D 56–21, and directions for using the Elliott cup in Proceedings A. S. T. M., 1917, part 1, p. 414.

but none of the varnish adheres to the finger. The varnish is considered to have dried hard when the pressure that can be exerted between the thumb and finger does not move the film or leave a mark which remains noticeable after the spot is lightly polished. If rapid light rubbing breaks the surface, the sample is considered not to have satisfactorily dried hard. In case the test shows time of setting to touch or drying hard more than 5 and 24 hours, respectively, two additional tests shall be run on different days, and if the varnish does not meet the above drying and hardening requirements on both of these additional tests it shall be considered unsatisfactory. In cases where different laboratories fail to agree on the drying test, due to different atmospheric conditions, and umpire tests are necessary, such tests shall be made in a well-ventilated room maintained at a temperature of 70° F. and relative humidity of 65 per cent saturation.

(*f*) Draft Test.—Flow the varnish on one of the standard tin panels and immediately place the panel in the direct draft of a small (8 or 10 inch) electric fan running at full speed. The panel should be placed approximately 2 feet from the fan in a nearly vertical position and at an angle of 45° to the line of the air current. Allow the panel to remain in this position for five hours, remove, and allow to harden overnight. The varnish shall show no dulling, crow's footing, or frosting. (This test shall be made under the same room and temperature condition noted under Drying Time.)

(*g*) Water Resistance.—Pour the varnish on two of the tin panels described above and allow to dry under the conditions described in paragraph (*e*) for 48 hours. Place one of these panels in a beaker containing about 2.5 inches of distilled water at room temperature (immersing the end of the panel which was uppermost during the drying period) and leave in water for 18 hours. The varnish shall show no whitening and no more than very slight dulling either when observed immediately after removing from the water or after drying for two hours. Place the other panel in a beaker containing about 2.5 inches of boiling distilled water (immersing the end of the panel which was uppermost during the drying period) and allow to remain in the boiling water for 15 minutes. The varnish shall show no whitening and no more than a very slight dulling either when observed immediately after removing from the water or after drying for two hours.

(*h*) Toughness.—The toughness of the varnish is determined by the Kauri reduction test, as follows: By proportionately reducing its toughness by the addition of a standard solution of "run-Kauri" gum in pure spirits of turpentine.

(*1*) *Preparation of the "Run Kauri."*—Arrange a distillation flask, water-cooled condenser, and a tared receiver on a balance. Place in the flask about one-third of its volumetric capacity of clear, bright hard pieces of Kauri gum broken to pea size. Carefully melt and distill until 25 per cent by weight of the gum taken is collected in the tared receiver. (At the end of the distillation the thermometer in the distillation flask with the bulb at the level of the discharging point of the flask should register about 316° C. (600° F.).) Pour the residue into a clean pan and when cold break up into small pieces.

(*2*) *Preparation of Standard "Run Kauri" Solution.*—Place a quantity of the small broken pieces of run Kauri together with twice its weight of freshly redistilled spirits of turpentine, using only that portion distilling over between 153° and 170° C. (308° and 338° F.) in a carefully tared beaker. Dissolve by heating to a temperature of about 149° C. (300° F.) and bring back to correct weight when cold by the addition of the amount of redistilled spirits of turpentine necessary to replace the loss by evaporation during the dissolving of the gum.

(*3*) *Reduction of the Varnish.*—Having carefully determined the nonvolatile content of the varnish according to the method under paragraph (*d*) of this specification, take 100 g of the varnish and add to it an amount of the standard run-Kauri solution equivalent to 50 per cent, by weight, of the nonvolatile matter in the varnish. Mix the varnish and the solution thoroughly.

(*4*) *Application of the Varnish.*—Flow a coat of the varnish thus reduced on one of the tin panels described above and let stand in a nearly vertical position at room temperature for one hour. Next place the panel in a horizontal position in a properly ventilated oven and bake for five hours at 95 to 100° C. Remove the panel from the oven and allow to cool at room temperature, preferably 24° C. (75° F.) for one hour.

(*5*) *Bending the Panel.*—Place the panel with the varnished side uppermost over a 3 mm (1/8-inch) rod, held firmly by suitable supports, at a point equally distant from the top and bottom edges of the panel and bend the panel double rapidly. The varnish must show no cracking whatsoever at the point of bending.

DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 111.

[2d edition, Issued June 24, 1922.]

UNITED STATES GOVERNMENT SPECIFICATION FOR FLAT INTERIOR LITHOPONE PAINT, WHITE AND LIGHT TINTS.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION No. 21.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

This specification covers ready-mixed lithopone paints, frequently known as flat, washable wall paint, in white and a variety of light tints. Paints under this specification are not intended for outside exposure; they shall dry to dead flat opaque coats that will adhere well to wood, metal, and plaster, stand washing with soap and water, and show no material change in color on exposure to light.

The paint shall be purchased by volume (231 cubic inches to the gallon).

109853°—22

(*a*) PIGMENT.—The pigment shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Lithopone	....	80
Zinc oxide	10	....
Tinting and extending pigments	10	....
Material soluble in water	0.8	....

NOTE.—The lithopone used must contain not less than 26 per cent of zinc sulphide and must not darken on exposure.

(*b*) LIQUID.—The liquid portion of the paint shall consist of treated drying oils or varnish, or a mixture thereof, and turpentine or volatile mineral spirits, or a mixture thereof, in such proportions as to insure not less than 25 per cent of nonvolatile vehicle. The nonvolatile vehicle shall dry to a tough and elastic film.

(*c*) PAINT.—The paint shall be well ground, shall not settle badly, cake, or thicken in the container, shall be readily broken up with a paddle to a smooth, uniform paint of brushing consistency, and shall dry within 18 hours to a dead flat finish without streaking, running, or sagging and free from laps and brush marks. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. After drying for not less than five days, marks made on the painted surface with a soft lead pencil (No. 2 Mogul) shall be easily removed by washing with soap and warm water without appreciably marring the paint surface. The weight per gallon shall be not less than 14½ pounds.

The paint shall consist of:

	Maximum.	Minimum.
	Per cent.	Per cent.
Pigment	72	68
Liquid (containing at least 25 per cent nonvolatile matter)	32	28
Water	1	....
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment)	3.0	....

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole. Whenever possible, an original unopened container shall be sent to the laboratory, and when this is for any reason not done the inspector shall determine by thor-

ough testing with a paddle or spatula whether the material meets the requirement regarding caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds. This sample shall be placed in a clean, dry metal or glass container, which it must nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION.

(*a*) Caking in Container.—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paint must be no more difficult to mix to a uniform consistency than a good grade of flat paint. The paint shall finally be thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paint shall be placed in a clean container and portions for the remaining tests promptly weighed out.

(*b*) Color.—Place some of the paint on a clean, clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(*c*) Weight per Gallon.—Weigh a clean, dry, 100 cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.33 gives the weight in pounds per gallon.

(*d*) Brushing Properties, Time of Drying, and Resistance to Washing.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let it stand for 18 hours. The paint should be dry and free from streaks.

Let the panel stand for five days, then make marks on it with a soft lead pencil (No. 2, Mogul) and wash these marks off with warm (75° C.) distilled water and white floating soap, using a sponge or soft rag. The marks must be removed by this treatment without appreciably marring the paint film.

(*e*) Fastness to Light.—Apply a sufficient number of coats of the paint to a ground-glass plate to completely hide the surface, cover half of this painted surface with opaque black paper, and exposure indoors in a well-lighted room for five days. Remove the black paper and examine the surface. The exposed portion should be no darker than the portion protected by the black paper.

(*f*) Water.—Mix 100 g of the paint in a 300 cc flask with 75 cc of toluol. Connect with a condenser and distil until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint. Material complying with the specification should yield less than 1.0 cc.

(*g*) Volatile Thinner.—Weigh accurately from 3 to 5 g of the paint into a tared flat-bottomed dish about 5 cm in diameter, spreading the paint over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate the loss in weight as percentage of water and volatile thinner, subtract from this the percentage of water (3 (*f*)), and report the remainder as volatile thinner.

(*h*) Percentage of Pigment.—Weigh accurately about 15 g of the paint into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment. Grind the pigment to a fine powder, pass through a No. 80 screen to remove any skins, and preserve in a stoppered bottle. Preserve the extracted vehicle for 3 (*j*).

(*i*) Percentage of Nonvolatile Vehicle.—Add together the percentages of water (3 (*f*)), of volatile thinner (3 (*g*)), and of pigment (3 (*h*)), and subtract the sum from 100. The remainder is the percentage of nonvolatile vehicle, which should be not less than one-third as large as the percentage of volatile thinner.

(*j*) Nature of Nonvolatile Vehicle.—Evaporate the extracted vehicle and extraction mixture from 3 (*h*) to about 5 cc Thoroughly clean with benzol a piece of bright sheet iron, tin plate, or terneplate. Spread a portion of the concentrated extracted vehicle on the sheet of metal, allow to dry for 30 minutes at room temperature in a vertical position, bake for three hours at 100 to 110° C. (212 to 221° F.), remove from the oven, and keep at room temperature for three days. Test the film with a knife blade at a place not less than 2.5 cm (1 inch) from the edge. The film should be tough and elastic; if it powders or if particles fly under the test, it will be considered brittle, which will be cause for rejection. The film must also stand light, vigorous rubbing with the finger without powdering or disintegrating.

(*k*) Coarse Particles and Skins.—Dry in an oven at 105 to 110° C. a No. 325 screen, cool, and weigh accurately. Weigh an amount of paint containing 10 g of pigment (see 3 (*h*)), add 50 cc of kerosene, mix thoroughly, and wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool, and weigh.

4. ANALYSIS OF PIGMENT.

Use the pigment extracted in 3 (*h*).

(*a*) Qualitative Analysis.—Make qualitative analysis following ordinary methods.

(*b*) Matter Soluble in Water.—Transfer 2.5 g of the pigment to a graduated 250 cc flask, add 100 cc of water, boil for five minutes, cool, fill to mark with water, mix, and allow to settle. Pour the supernatant liquid through a dry filter paper and discard the first 20 cc. Then evaporate 100 cc of the clear filtrate to dryness in a weighed dish, heat for one hour at 105 to 110° C., cool, and weigh. The residue should not exceed 0.008 g.

(*c*) Barium Sulphate and Siliceous Material.—Transfer 1 g of pigment to a porcelain casserole or dish, moisten with a few drops of alcohol, add 40 cc of hydrochloric acid (1.1, specific gravity), cover, and boil to expel hydrogen sulphide; remove the cover and evaporate to dryness on the steam bath, moisten with hydrochloric acid, dilute with water, filter through paper, and wash with dilute hydrochloric acid and then with hot water until

the washings are free from zinc and chlorine. Ignite and weigh the residue, which will be barium sulphate and siliceous material.

Mix the ignited residue with about 10 times its weight of anhydrous sodium carbonate (grind the mixture in an agate mortar if necessary), fuse the mixture in a covered platinum crucible, heating about one hour. Let cool, place the crucible and cover in a 250 cc beaker, add about 100 cc of water, and heat until the melt is disintegrated. Filter on paper (leaving the crucible and cover in the beaker) and wash the beaker and filter thoroughly with hot water to remove soluble sulphates. Place the beaker containing the crucible and cover under the funnel, pierce the filter with a glass rod, and wash the carbonate residue into the beaker by means of a jet of hot water. Wash the paper with hot dilute hydrochloric acid (1:1), and then with hot water. If the carbonate residue is not completely dissolved, add sufficient dilute hydrochloric acid to effect solution, and remove the crucible and cover, washing them with a jet of water. Heat the solution to boiling and add 10 to 15 cc of dilute sulphuric acid, and continue the boiling for 10 or 15 minutes longer. Let the precipitate settle, filter on a weighed Gooch crucible, wash with hot water, ignite, cool, and weigh as $BaSO_4$. Subtract from the result of the previous determination to obtain the siliceous material.

(*d*) Total Zinc Calculated as Zinc Oxide.—With material containing no interfering elements (iron, for example) weigh accurately about 1 g of pigment, transfer to a 400 cc beaker, moisten with alcohol, add 30 cc of hydrochloric acid (1:2), boil for two to three minutes, add 200 cc of water and a small piece of litmus paper; add strong ammonia until slightly alkaline, render just acid with hydrochloric acid, then add 3 cc of strong hydrochloric acid, heat nearly to boiling, and titrate with standard ferrocyanide as in standardizing that solution (see Reagents). Calculate total zinc as zinc oxide.

When iron or other interfering elements are present (see 4 (*a*)), take the filtrate containing the zinc from 4 (*c*), add a slight excess of bromine water and 2 g ammonium chloride, heat to nearly boiling, add an excess of ammonia, heat for about two minutes, filter, dissolve the precipitate in hydrochloric acid, add 2 g of ammonium chloride, and reprecipitate with ammonia as above. Filter, wash the precipitate with hot 2 per cent ammonium-chloride solution, unite the two filtrates, and determine zinc as above.

(*e*) Zinc Oxide.—Weigh accurately 2.5 g of pigment, transfer to a 250 cc graduated flask, moisten with a few drops of alcohol, add about 200 cc of 1 to 3 per cent acetic acid, shake vigorously and let stand for 30 minutes, shaking once every five minutes. Fill to the mark with 1 to 3 per cent acetic acid, mix, filter through a dry paper, discard the first 25 cc and determine zinc in 100 cc of the filtrate (corresponding to 1 g) as in 4 (*d*). Calculate the percentage of zinc oxide.

(*f*) Calculations.—Subtract the percentage of zinc oxide (4 (*e*)) from the percentage of total zinc as zinc oxide (4 (*d*)) and multiply the remainder by 1.2 to convert to percentage of zinc sulphide. In case the percentage of barium sulphate (4 (*c*)) is not more than 2.86 times as great as the percentage of zinc sulphide, add the two together and call the sum the percentage of lithopone. If the percentage of barium sulphate is greater than this amount, take 2.86 times the percentage of zinc sulphide as the percentage of barium sulphate to be included in the percentage of lithopone and include the remainder in the percentage of tinting and extending pigments. Subtract the sum of the percentage of zinc oxide (4 (*e*)), lithopone, and matter soluble in water (4 (*b*)) from 100. Call the remainder percentage of tinting and extending pigments.

5. REAGENTS.

(*a*) Extraction Mixture.—

10 volumes ether (ethyl ether).
6 volumes benzol.
4 volumes methyl alcohol.
1 volume acetone.

(*b*) One to Three Per Cent Acetic Acid.—Dilute 20 cc glacial acetic acid to 1,000 cc with distilled water.

(*c*) Uranyl Indicator for Zinc Titration.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*d*) Standard Potassium Ferrocyanide.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400 cc beaker. Dissolve in 10 cc of hydrochloric acid and 20 cc of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and then 3 cc.

of strong hydrochloric acid. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing one minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume, and acidity as obtain when the sample is titrated.

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DEPARTMENT OF COMMERCE.

BUREAU OF STANDARDS.

S. W. STRATTON, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 117.

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UNITED STATES GOVERNMENT SPECIFICATION FOR INTERIOR VARNISH.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION No. 22.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

CONTENTS.

1. GENERAL.

The varnish shall be suitable for general interior use, including both rubbed and unrubbed finish, exclusive of floors. It must be capable of easy application with a brush in the ordinary manner according to the rules of good standard practice, must flow out to a good level coat free from runs, sags, pits, or other defects, and dry with reasonable promptness to a hard, somewhat elastic glossy coating which can be rubbed in 48 hours or less. The manufacturer is given wide latitude in the selection of raw materials and processes of manufacture, so that he may produce a varnish of the highest quality. The varnish must meet the following requirements:

APPEARANCE.—Clear and transparent.

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COLOR.—Not darker than a solution of 3 g of potassium dichromate in 100 cc of pure sulphuric acid, specific gravity 1.84.

FLASH POINT (CLOSED-CUP).—Not below 30° C. (85° F.).

NONVOLATILE MATTER.—Not less than 45 per cent by weight.

SET TO TOUCH.—In not more than 4 hours.

DRY HARD.—In not more than 24 hours.

DRY TO RUB.—In not more than 48 hours.

TOUGHNESS.—Film on metal must stand rapid bending over a rod 3 mm (1/8 inch) in diameter.

WORKING PROPERTIES.—Must have good brushing, flowing, covering, leveling, and rubbing properties; and must show no impairment of luster or other defect when used where natural or illuminating gases are burned or when subjected to air currents during the process of drying or application.

WATER RESISTANCE.—The dried film must stand application of cold water for not less than 18 hours without whitening or showing other visible defect.

NOTE.—Deliveries will, in general, be sampled and tested, by the following methods, but the purchaser reserves the right to use any available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall be taken as representative of the whole. Whenever possible, an original unopened container shall be sent to the laboratory, and when for any reason this is not done, the inspector shall thoroughly mix the contents of the container sampled, transfer not less than 1 quart to a clean dry glass bottle or tin can which must be nearly filled with the sample, securely stoppered with a new clean cork or well-fitting cover, or cap, sealed, and distinctly labeled by the inspector.

The inspector should take a duplicate from the container sampled to be held for check in case of dispute, and, when requested, should take a sample for the seller.

3. LABORATORY EXAMINATION.

The tin panels used in the following tests shall be cut from bright tin plate weighing not more than 25 g nor less than 19 g per square decimeter (0.51 to 0.39 pound per square foot). (Commercial No. 31 gage bright tin plate should weigh about 0.44 pound per square foot. It is important that the tin plate used shall be within the limits set.)

(*a*) APPEARANCE.—Pour some of the thoroughly mixed sample into a clear glass bottle or test tube and examine by transmitted light. The varnish must be clear and transparent.

(*b*) COLOR.—Prepare a standard color solution by dissolving 3 g of pure powdered potassium dichromate in 100 cc of pure concentrated sulphuric acid of specific gravity 1.84. Gentle heat may be used if necessary to perfect the solution of the dichromate. The standard color solution and a sample of the varnish to be tested shall be placed in clear, thin-walled glass tubes of the same diameter. The color comparison shall be made by placing the tubes close together and looking through them by transmitted light. The tubes used for this test should be 1.5 to 2.0 cm (5/8 to $\frac{13}{16}$ inch) in diameter and shall be filled to a depth of at least 2.5 cm (1 inch). (Since the potassium dichromate-sulphuric acid must be freshly made for this color comparison, it is frequently more convenient to compare samples with a permanently sealed tube of varnish which has previously been found to be slightly lighter in color than the standard solution of 3 g dichromate in sulphuric acid. When samples are found to be darker than this standard tube of varnish, the dichromate standard should be made up for final decision.)

(*c*) FLASH POINT.—Determine with either the Tag or Elliott closed-cup tester. The former is preferred.[1]

(*d*) NONVOLATILE MATTER.—Place a portion of the sample in a stoppered bottle or weighing pipette. Weigh container and sample. Transfer about 1.5 g of the sample to a weighted flat-bottomed metal dish about 8 cm diameter (a friction-top can plug). Weigh container again and by difference calculate the exact weight of the portion of sample transferred to the weighed dish. Heat dish and contents in an oven maintained at 105 to 110° C. (221 to 230° F.) for three hours. Cool and weigh. From the weight of the residue left in the dish and weight of the sample taken, calculate the percentage of nonvolatile residue.

(*e*) DRYING TIME.—Pour the varnish on a clean glass or bright tin plate not less than 15 cm (6 inches) long and 10 cm (4 inches) wide. Place the plate in a nearly vertical position in a well-ventilated room but not in the direct rays of the sun. The temperature of the room should be from 21 to 32° C. (70 to 90° F.). The film is tested at points not less than 2.5 cm (1 inch) from the edges of the film by touching lightly with the finger. The varnish is

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[1] Directions for using the Tag tester may be found in A. S. T. M. Standards D 56–21, and directions for using the Elliott cup in Proceedings A. S. T. M., 1917, pt. 1, p. 414.

considered to have set to touch when gentle pressure of the finger shows a tacky condition but none of the varnish adheres to the finger. The varnish is considered to have dried hard when the pressure that can be exerted between the thumb and finger does not move the film or leave a mark which remains noticeable after the spot is lightly polished. If rapid light rubbing breaks the surface, the sample is considered not to have satisfactorily dried hard. In case the test shows time of setting to touch or drying hard more than 4 and 24 hours, respectively, two additional tests shall be run on different days and if the varnish does not meet the above drying and hardening requirements on *both* of these additional tests it shall be considered unsatisfactory. In cases where different laboratories fail to agree on the drying test, due to different atmospheric conditions, and umpire tests are necessary, such tests shall be made in a well-ventilated room maintained at a temperature of 70° F. and relative humidity of 65 per cent saturation.

(*f*) Toughness.—Thoroughly clean with benzol a sheet of bright tin 7.5 by 13 cm (about 3 by 5 inches). Flow the varnish on one side of the tin plate and set in a vertical position in a well-ventilated room, not in the direct rays of the sun, at a temperature not below 21° C. (70° F.).

After the varnish on the tin plate has dried for 48 hours bring to a temperature between 21 and 24° C. (70 to 75° F.), and with the varnish film on the outside, bend rapidly over a rod 3 mm (1/8 inch) in diameter. The film must show no evidence of cracking or flaking.

(*g*) Water Resistance.—Prepare a panel as in (*f*) and let it dry in a well-ventilated room for 48 hours. Place the panel in a beaker containing about 2.5 inches of distilled water at room temperature (immersing the end of the panel which was uppermost during the drying period) and leave in water for 18 hours. The varnish shall show no whitening and no more than a very slight dulling when observed after removing the panel from the water and drying for 2 hours.

(*h*) Flowing and Rubbing Properties.—Thoroughly clean with benzol a glass plate about 15 by 20 cm (6 by 8 inches). Flow the varnish so as to entirely cover one side of the plate and stand in a nearly vertical position with the long edge horizontal for 8 minutes. Then draw lightly a 25 mm (1 inch) section of a hard-rubber comb (having 8 to 10 teeth to the centimeter) horizontally across the varnish surface, first 2 cm from the bottom and then 2 cm

from the top of the plate. Let panel stand in the same position for 20 minutes longer, then lay flat. An exaggerated condition of a dusty room shall be created by rubbing some cotton batting between the hands immediately over the panel. Let panel dry for a total of 48 hours in a well-ventilated room. If the comb marks show at this time, the varnish shall be rejected. If no comb marks show, the surface shall then be rubbed with pumice flour, water, and a felt pad with long, even, firm strokes back and forth in one or another direction, but not in circles, until every portion of the panel has been rubbed. Most of the pumice will then be removed from the pad and panel, and the varnish film given a "water rub" with the pad.

A satisfactory rubbing varnish in the above test will yield a smooth, dull film even at those places where the dust particles have been encrusted in the film, and shall show no spots where the pumice has been ground into and become attached to the film, nor show any other evidence of gumming. No sweating shall occur anywhere on the film in 18 hours after rubbing.

(*i*) GAS TEST.—*Apparatus*.—The necessary apparatus consists of a glass bell jar approximately 20 cm (8 inches) in diameter and 30 cm (12 inches) in height, inside dimensions, having a ground-glass rim; a ground-glass base plate of suitable size; a small, kerosene glowlamp without chimney, or a small alcohol lamp filled with kerosene, using a round wick not over 6 mm (¼ inch) in diameter and adjusted to give a flame 2 cm (4/5 inch) in height. A wire or a light wooden frame is fitted inside the jar and provided with a support for holding a disk of tin plate 15 cm (6 inches) in diameter in a horizontal position 5 cm (2 inches) above the wick of the lamp. The frame must also be provided with several other supports above this disk for holding in a horizontal position the various varnished panels under test. The test panels consist of semicircular pieces of bright tin plate approximately 15 cm (6 inches) in diameter.

The form and arrangement of the above apparatus is designed to provide an even distribution of the products of combustion over the test panels.

Method.—First determine the normal time required for the varnish under examination to set to touch at room temperature. Divide this time by five to arrive at the different drying periods at which the varnish is to be tested in the gas tester. Thus, if a varnish sets to touch in five hours, samples should be tested for resistance to gas at drying periods of one, two, three, and four

hours; it is needless to use the fifth or five-hour period for the above varnish, as a varnish which has set to touch is practically immune to injury from gas fumes. Similarly a varnish which sets to touch in one hour should be tested for resistance to gas at drying periods of 12, 24, 36, and 48 minutes.

Example.—A varnish which sets to touch in five hours is tested as follows:

First, clean two of the semicircular, bright, tin-plate panels carefully with benzol. Flow the varnish on one-half of panel No. 1 at, say, 10 a. m., and allow to drain in a nearly vertical position at room temperature. At 11 a. m., flow the varnish on the other half of panel No. 1; allow to drain as before. At 12 m. varnish one-half of panel No. 2, and at 1 p. m. varnish the other half, as above. At 2 p. m. place the two panels close together in a horizontal position on the upper supports of the frame. Light the lamp and set it under the circular tin. Place the bell jar in position, centering it as nearly as possible, properly seated on the ground-glass plate. If the chamber is tight and lamp properly adjusted, the flame will be extinguished in about four minutes. After the panels have been in the chamber for half an hour, remove the bell jar and examine the varnished panels for gas effects.

The varnish on all four sections should remain bright and clear without trace of pitting, "crow's footing," frosting, or other defects.

4. BASIS OF PURCHASE.

Varnish shall be purchased by volume, the unit being a gallon of 231 cubic inches at 15.5° C. (60° F.). The volume may be determined by measure, or, in case of large deliveries, it may be easier to determine the net weight and specific gravity at 15.5/15.5° C. (60/60° F.) of the delivery. The weight per gallon in pounds can then be determined by multiplying the specific gravity by 8.33. The net weight in pounds divided by the weight per gallon gives the number of gallons.

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DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

NO. 86

[Issued February 16, 1920]

RECOMMENDED SPECIFICATIONS FOR TURPENTINE

(Gum Spirits and Wood Turpentine)

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, OCTOBER 27, 1919. P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; H. E. SMITH, U. S. RAILROAD ADMINISTRATION, SECRETARY.

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Railroad Administration, the Panama Canal, and the Educational Bureau of the Paint Manufacturers Association of the United States. The committee submitted a preliminary draft of the specification to a large number of representatives of the naval-stores industries and the paint and varnish industries, and gave careful consideration to the replies which were received in time.]

CONTENTS

1. GENERAL

These specifications apply both to the turpentine which is distilled from pine oleoresins, commonly known as gum spirits or spirits of turpentine, and to turpentine commonly known as wood turpentine, which is obtained from resinous wood, whether by steam or by destructive distillation. When ordering under these specifications, the purchaser shall specify whether (*a*) gum spirits or (*b*) wood turpentine is desired. When wood turpentine is specified, it may be stated whether steam or destructively distilled wood turpentine shall be furnished.

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Turpentine shall be pure and conform to the following requirements:

APPEARANCE.—Shall be clear and free from suspended matter and water.

COLOR.—Shall be "standard" or better.

ODOR.—Shall be characteristic of the variety of turpentine specified and, if desired, shall conform to the odor of the sample agreed upon.

	Maximum	Minimum
Specific gravity, 15.5/15.5° C	0.875	0.862
Refractive index at 20° C	1.478	1.468
Residue after polymerization with 38 N H_2SO_4:		
Gum spirits—		
Volume (per cent)	2.0	
Refractive index at 20° C		1.500
Wood turpentine—		
Volume (per cent)	2.5	
Refractive index at 20° C		1.495
Initial boiling point at 760 mm pressure	160° C	150° C
Distilling below 170° C at 760 mm pressure (per cent)		90

2. DETECTION AND REMOVAL OF SEPARATED WATER

Draw a portion by means of a glass or metal container with a removable stopper or top, or with a "thief," from the lowest part of the container, or by opening the bottom valve of the perfectly level tank car. If water is found to be present, draw it all out, record the quantity, and deduct it from the total volume of liquid delivered.

3. SAMPLING

The method of sampling given under (*a*) should be used whenever feasible. When method (*a*) is not applicable, method (*b*), (*c*), or (*d*) is to be used according to the special conditions that obtain.

(*a*) **While Loading Tank Car or While Filling Containers for Shipment.**—Samples shall be drawn by the purchaser's inspector at the discharge pipe where it enters the receiving vessel or vessels. The composite sample shall be not less than 5 gallons and shall consist of small portions of not more than 1 quart each taken at regular intervals during the entire period of loading or filling.

The composite sample thus obtained shall be thoroughly mixed and from it three samples of not less than 1 quart each shall be placed in clean, dry, glass bottles or tin cans, which must be nearly filled with the sample and securely stoppered with new, clean corks or well-fitting covers or caps. These shall be sealed and distinctly labeled by the inspector; one shall be delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(*b*) **From Loaded Tank Car or Other Large Vessel.**—The composite sample taken shall be not less than 5 gallons and shall consist of numerous small samples of not more than 1 quart each taken from the top, bottom, and intermediate points by means of a metal or glass container with removable stopper or top. This device, attached to a suitable pole, is lowered to the various desired depths, when the stopper or top is removed and the container allowed to fill. The sample thus obtained is handled as in (*a*).

(*c*) **Barrels and Drums.**—Barrels and drums shall be sampled after gaging contents. Five per cent of the packages in any shipment or delivery shall be represented in the sample. Thoroughly mix the contents of each barrel to be sampled by stirring with a clean rod and withdraw a portion from about the center by means of a "thief" or other sampling device. The composite sample thus obtained shall be not less than 3 quarts, shall consist of equal portions of not less than one-half pint from each package sampled, and shall be handled as in (*a*). Should the inspector suspect adulteration, he shall draw the samples from the suspected packages.

(*d*) **Small Containers, Cans, Etc., of 10 Gallons or Less.**—These should be sampled, while filling, by method (*a*) whenever possible; but in case this is impossible the composite sample taken shall be not less than 3 quarts. This shall be drawn from at least five packages (from all when fewer), and in no case from less than 2 per cent of the packages. The composite sample thus taken shall be thoroughly mixed and subdivided as in (*a*).

4. LABORATORY EXAMINATION

Samples will, in general, be tested by the following methods; but the purchaser reserves the right to apply any additional tests or use any available information to ascertain whether the material meets the specifications:

(*a*) **Appearance.**—Examine to determine compliance with the specifications.

(*b*) **Color.**—Fill a 200 mm perfectly flat-bottomed colorimeter tube, graduated in millimeters, to a depth of from 40 to 50 mm with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter, place a No. 1 yellow Lovibond glass and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm or more, the turpentine is "standard" or better.

(*c*) **Odor.**—Determine by comparison with several samples of known purity, which have been kept in the dark in completely filled, well-stoppered bottles and are free from separated water.

(*d*) **Specific Gravity.**—Determine at 15.5/15.5° C, in a pycnometer accurately standardized and having a capacity of at least 25 cc, or by any other equally accurate method.

(*e*) **Refractive Index.**—Determine refractive index at 20° C with an accurate instrument. When the refractive index is determined at any other temperature, the readings obtained shall be corrected to 20° C by adding to or by subtracting from the actual reading 0.00045 for each degree centigrade that the temperature at which the determination was made is, respectively, above or below 20° C.

(*f*) **Distillation.**—APPARATUS.[1]—*Condenser.*—The type of apparatus (see Fig. 1) adopted by the American Society for Testing Materials for the distillation of paint thinners other than turpentine, substituting for the thermometer there described[2] an immersed thermometer such as is described below, is preferred. In case the A. S. T. M. distillation apparatus is not available, use an ordinary straight glass-tube condenser, about 22 inches long, with 16 inches in contact with the cooling water. The end of the condenser tube should be fitted with an adapter or should be bent down to a nearly vertical position, and the tip should be cut off or ground down at an acute angle. The tip should extend a short distance into the receiving cylinder.

Flask.—Comparable results can be obtained only by using flasks of the same dimensions. The distilling flask used shall be the standard Engler flask, as used for petroleum distillation, having the following dimensions: Diameter of bulb, 6.5 cm; cylindrical neck, 15 cm long, 1.6 cm internal diameter; side or vapor tube, 10 cm long, 0.6 cm external diameter, attached to

[1] Fig. 1.

[2] A. S. T. M. Standards, p. 607; 1918.

neck at an angle of 75°, so that when the flask contains its charge of 100 cc of oil the surface of the liquid shall be 9 cm below the bottom of the junction of the side tube and neck.

Support for Flask.—Support the flask on a plate of asbestos 20 cm in diameter, having an opening 4 cm in diameter in its center, and heat with an open flame. Surround the flask and burner with a shield to prevent fluctuation in the temperature of the neck of the flask. Or, support the flask in a metal cup, 15 to 20 cm in diameter, containing high-boiling mineral oil or glycerin

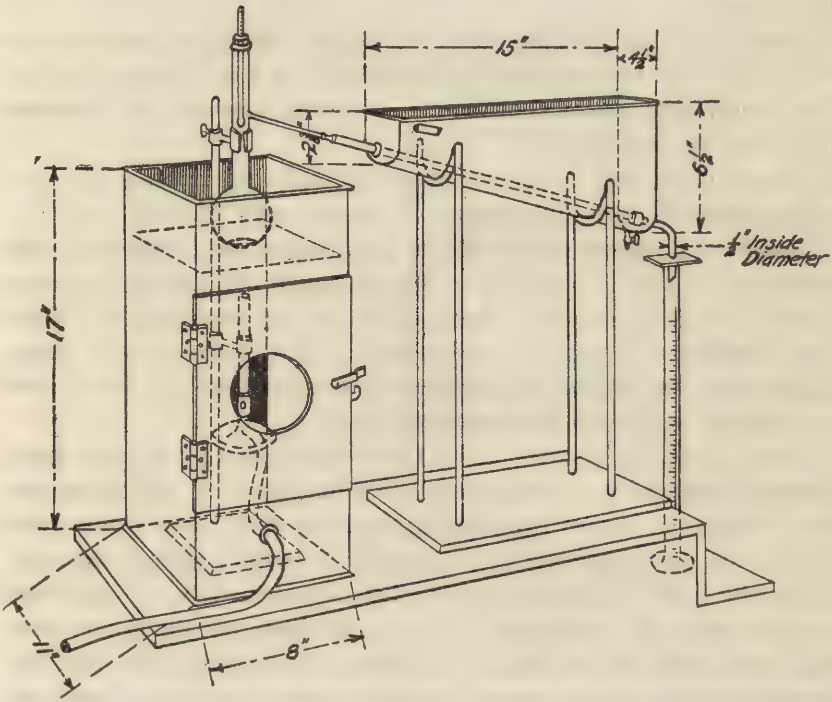

FIG. 1.—*Distillation apparatus*

and fitted with a concave cover having in the center a circular opening 5½ to 6 cm in diameter. In all cases take the necessary precautions to prevent fluctuation in temperature in the neck of the flask.

Thermometer.—The thermometer used for turpentine distillation shall conform to the following specifications:

It shall be graduated from 145° to at least 200° C in 0.2° intervals. Thermometers graduated above 200° C may be used, provided they also comply with the following requirements: Length, bottom of thermometer to 175° mark, not more than 8 nor less than

6.5 cm. Length, top of bulb to 145° mark, not less than 1.5 cm. Length, 145 to 175° mark, not more than 6 cm.

The thermometer shall be made of suitable thermometric glass and thoroughly annealed, so that the scale errors will not increase after continued heating.

The thermometer shall be filled above the mercury with an inert gas, with sufficient pressure above the mercury column to prevent breaking of the column. It shall have a reservoir at the top, so that the pressure will not become excessive at the highest temperature.

Every fifth graduation shall be longer than the intermediate ones, and the marks shall be numbered at each interval of 5°. The graduation marks shall be clear-cut and fine and the numbering clear-cut and distinct.

The error at any point on the scale shall not exceed ±0.5° C when tested for total immersion of the mercury column.

Receiving Cylinder.—Collect the distillate in an accurately graduated 50 or 100 cc cylinder. The so-called normal or precision cylinder of 50 cc capacity, having an internal diameter of 1.5 cm and graduated in 0.2 cc, is preferred. If a cylinder with larger inside diameter is used, a pasteboard cover should be placed over the top and surround the condenser tube.

Operation.—Place 100 cc of the turpentine and several small pieces of pumice (or glass) in the distilling flask, fit the thermometer so that the top of the mercury bulb is level with the bottom of the side tube, and the 175° C (347° F) mark is below the cork. Place the flask in position on the asbestos board or oil bath and connect with the condenser. Apply the heat cautiously at first, and, when distillation begins, regulate the heat so that the turpentine distills at the rate of not less than 4 nor more than 5 cc per minute (approximately two drops per second). The initial boiling point is the thermometer reading at the instant when the first drop falls from the end of the condenser. Discontinue distillation when the temperature reaches 170.0° C (338° F), or an equivalent thereof, depending on the atmospheric pressure, as outlined below; let the condenser drain and read the percentage distilled.

The percentage distilled below successive selected temperatures and the temperature at which each successive 10 cc. distills may also be determined, if desired, making the necessary correction of the temperature for variations in atmospheric pressure.

Correction for Variation in Atmospheric Pressure.—Since distillation results are comparable only when obtained under exactly the same pressure conditions, turpentine shall be distilled at that pressure which, at room temperature, is equivalent to a pressure of 760 mm of mercury at 0° C. Whenever the atmospheric pressure after correcting to 0° C is other than 760 mm, a correction must be made. Since alteration of the pressure in the distilling system requires rather complicated apparatus, it is simpler to alter the temperature observation points to correspond to the prevailing pressure.

To determine what the atmospheric pressure at the prevailing room temperature, or at the temperature of the barometer, would be at 0° C, read the barometer and thermometer alongside when about to begin distillation. Refer to Table 1, page 11. Under the column nearest the observed pressure reading, and on the line nearest the observed temperature of the barometer will be found the correction which must be subtracted from the observed pressure reading to obtain the equivalent, or true, reading at 0° C.

The distilling temperature of turpentine is affected plus (+) or minus (−) 0.057° C for each millimeter variation of the barometer above or below the normal 760 mm at 0° C.[3] If the barometer reading, after correcting to 0° C, is below 760 mm, the turpentine will distill at a slightly lower temperature than under normal pressure. Therefore, the temperature recorded at the beginning of distillation (and any others observed during the course of the distillation) must be corrected to get its equivalent at normal pressure. The final temperature observation point (170° C of the specifications) must be altered accordingly to get its equivalent at the pressure (corrected to − ° C) at which distillation is made.

For example, if the barometer reading, after correcting to 0° C, is 750 mm, the correction of the observed initial distilling temperature will be 0.057×10 mm $= 0.6°$ C approximately. If the reading of the thermometer when the turpentine begins to distill is 155.6° C, the corrected initial distilling temperature will be $155.6° + 0.6° = 156.2°$ C. Furthermore, the temperature observation point at end of distillation (170.0° C at 760 mm) must be altered to the same extent. Since the turpentine is distilling 0.6° C below what it would at normal pressure, distillation must

[3] Landolt-Börnstein Physikalisch-Chemische Tabellen, Ed. 4, Table 127, p. 435.

be discontinued at 0.6° C below the specified limit of 170.0° C to determine the percentage distilling below 170.0° C.

If the barometer reading corrected to 0° C is above 760 mm, subtract the temperature correction from the observed thermometer reading to determine the initial distilling point, and continue distillation to 170.0° C plus the correction to determine the percentage distilling below 170.0° C.

(*g*) **Polymerization.**—Place 20 cc of 38 *N* (equivalent to 100.92 per cent H_2SO_4) sulphuric acid in a graduated, narrow-necked Babcock flask, stopper, and place in ice water to cool. Add slowly, from a pipette, 5 cc of the turpentine to be examined. Gradually mix the contents, keeping warm, but being very careful that the temperature does not rise above 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the flask in a water bath and heat at 60 to 65° C for not less than 10 minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking for one-half minute each time, six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck and centrifuge from four to five minutes at not less than 1200 r. p. m., or for 15 minutes at 900 r. p. m., or allow to stand, lightly stoppered, for 12 hours. Calculate the percentage, note the consistency and color, and determine the refractive index (at 20° C) of the unpolymerized residue. The consistency should be viscous and the color straw or darker.

Reagent for Testing.—In a weighed glass-stoppered bottle (the regular 2½-liter acid bottle is of a convenient size) mix ordinary concentrated sulphuric acid (sp. gr. 1.84) with fuming sulphuric acid. If the fuming acid used contains 50 per cent excess SO_3, the ratio of one part, by weight, of the former to three-fourths of a part, by weight, of the latter will give a mixture slightly stronger than the required strength. To determine the exact strength of this mixture in terms of H_2SO_4, weigh exactly, in a weighing pipette of about 10 cc capacity, approximately 20 g of the acid. Allow it to flow down the sides of the neck into a 1000-cc volumetric flask containing about 200 cc of distilled water. When the pipette has drained, wash all traces of the acid remaining in the pipette into the flask, taking precautions to prevent loss of SO_3, and make up to the mark. Titrate

20-cc portions, drawn from a burette, against half normal alkali. Calculate the concentration in terms of the percentage of H_2SO_4 in the sample taken.

In the same way determine the percentage of H_2SO_4 in the stock of ordinary concentrated acid (sp. gr. 1.84). From these data calculate the quantity of the latter which must be added to the quantity of mixed acid in the weighed bottle to bring it to a concentration, in terms of H_2SO_4, of 100.92 per cent.

After adjusting the concentration by the addition of the ordinary sulphuric acid, thoroughly shake the bottle of mixed acid and again determine its concentration. The allowable variation is ± 0.05 per cent H_2SO_4. Finally as a check run a polymerization test on gum turpentine known to be pure. The residue should fall below 2 per cent.

Special precautions must be taken to prevent dilution of this acid by the absorption of atmospheric moisture. The arrangement shown in Fig. 2 is most suitable for storing and delivering measured quantities of this reagent.

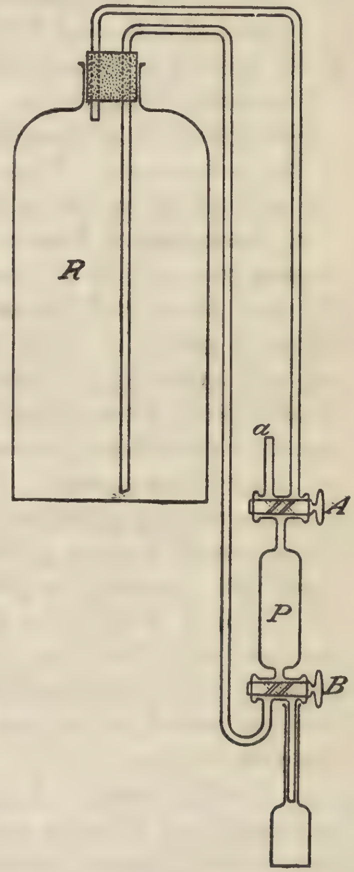

FIG. 2.—*Acid bottle and pipette*

With the three-way stopcocks *A* and *B* in the position shown, acid is siphoned into the pipette *P*, the displaced air passing into *R*. To empty the pipette, *A* and *B* are turned to the position shown by the broken lines, air passing in at *a*. The acid adhering to the walls of the pipette dries this air so that when it passes into *R* on again filling the pipette there is no accumulation of moisture in the acid remaining in the reservoir. If such arrangement is not to be had, the acid should be kept in well-fitting glass-stoppered bottles of not more than one-half liter capacity.

5. BASIS OF PURCHASE

(*a*) **Unit.**—Turpentine shall be purchased (*a*) by volume, the unit being a gallon of 231 cubic inches at 15.5° C (60° F), or (*b*) by weight. A gallon of turpentine at 15.5° C (60° F) weighs 7.19 to 7.30 pounds. The exact weight in pounds per gallon of any sample can be determined by multiplying the specific gravity at 15.5/15.5° C (60/60° F) by 8.34. Example: If the specific gravity at 15.5° C is 0.8642, the weight per gallon at this temperature will be $0.8642 \times 8.34 = 7.207$ pounds.

When purchased by weight, quotations shall be by the pound or by the 100 pounds. The request for bids will state whether quotations shall be by the gallon, pound, or 100 pounds.

(*b*) **Correction of Volume.**—The gallonage paid for shall be the volume corrected to a standard temperature of 15.5° C (60° F). The correction shall be deducted from (when the temperature of gaging is above 15.5° C) or added to (when the temperature of gaging is below 15.5° C) the gallonage as gaged. Such deduction or addition shall be computed on the basis of a coefficient of expansion for turpentine of 0.000945 per degree centigrade (or 0.000525 per degree Fahrenheit). Example: If the temperature at which the turpentine is gaged is 75° F and the volume delivered (at that temperature) is 8000 gallons, then $0.000525 \times 15° \times 8000$ gallons equals the quantity in gallons which must be subtracted from 8000 gallons to give the true gallonage at 60° F, or, if the temperature at which the turpentine is gaged is 10° C, then $0.000945 \times 5.5° \times 8000$ gallons equals the quantity in gallons which must be added to the gaged volume of 8000 gallons to give the true gallonage at 15.5° C.

(*c*) **Certification.**—Turpentine delivered in barrels, drums, or tank cars shall either be accompanied by an official gager's certificate showing the net contents of each container and also the temperature of contents at time of gaging, or shall be subject to gaging by the purchaser's inspector. In the absence of a statement of the temperature at the time of gaging on the official gager's certificate, or in case the barrels show evidence of loss by leakage or other shortage, the delivery shall be subject to reinspection and regaging by the purchaser's inspector.

TABLE 1.—Correction to Barometer Readings [a]

[From circular F, instrument division, Weather Bureau, U. S. Department of Agriculture]

Temperature, °C	Observed reading of barometer, in millimeters														
	640	650	660	670	680	690	700	710	720	730	740	750	760	770	780
15.0	1.56	1.59	1.61	1.64	1.66	1.69	1.71	1.74	1.76	1.78	1.81	1.83	1.86	1.88	1.91
16.0	1.67	1.69	1.72	1.75	1.77	1.80	1.83	1.85	1.88	1.90	1.93	1.96	1.98	2.01	2.03
17.0	1.77	1.80	1.83	1.86	1.88	1.91	1.94	1.97	1.99	2.02	2.05	2.08	2.10	2.13	2.16
18.0	1.88	1.91	1.93	1.96	1.99	2.02	2.05	2.08	2.11	2.14	2.17	2.20	2.23	2.26	2.29
19.0	1.98	2.01	2.04	2.07	2.10	2.13	2.17	2.20	2.23	2.26	2.29	2.32	2.35	2.38	2.41
20.0	2.08	2.12	2.15	2.18	2.21	2.25	2.28	2.31	2.34	2.38	2.41	2.44	2.47	2.51	2.54
21.0	2.19	2.22	2.26	2.29	2.32	2.36	2.39	2.43	2.46	2.50	2.53	2.56	2.60	2.63	2.67
22.0	2.29	2.33	2.36	2.40	2.43	2.47	2.51	2.54	2.58	2.61	2.65	2.69	2.72	2.76	2.79
23.0	2.40	2.43	2.47	2.51	2.54	2.58	2.62	2.66	2.69	2.73	2.77	2.81	2.84	2.88	2.92
24.0	2.50	2.54	2.58	2.62	2.66	2.69	2.73	2.77	2.81	2.85	2.89	2.93	2.97	3.01	3.05
25.0	2.60	2.64	2.68	2.72	2.77	2.81	2.85	2.89	2.93	2.97	3.01	3.05	3.09	3.13	3.17
26.0	2.71	2.75	2.79	2.83	2.88	2.92	2.96	3.00	3.04	3.09	3.13	3.17	3.21	3.26	3.30
27.0	2.81	2.85	2.90	2.94	2.99	3.03	3.07	3.12	3.16	3.20	3.25	3.29	3.34	3.38	3.42
28.0	2.91	2.96	3.00	3.05	3.10	3.14	3.19	3.23	3.28	3.32	3.37	3.41	3.46	3.51	3.55
29.0	3.02	3.06	3.11	3.16	3.21	3.25	3.30	3.35	3.39	3.44	3.49	3.54	3.58	3.63	3.68
30.0	3.12	3.17	3.22	3.27	3.32	3.36	3.41	3.46	3.51	3.56	3.61	3.66	3.71	3.75	3.80
31.0	3.22	3.27	3.32	3.37	3.43	3.48	3.53	3.58	3.63	3.68	3.73	3.78	3.83	3.88	3.93
32.0	3.33	3.38	3.43	3.48	3.54	3.59	3.64	3.69	3.74	3.79	3.85	3.90	3.95	4.00	4.05
33.0	3.43	3.48	3.54	3.59	3.64	3.70	3.75	3.81	3.86	3.91	3.97	4.02	4.07	4.13	4.18

[a] These corrections apply to a mercurial barometer with brass scale. They can, however, be used for a mercurial barometer with glass scale, since the errors introduced thereby are negligible as applied to the work contemplated in this Circular. For exact correction to be applied to such a barometer see Smithsonian Physical Tables, p. 119; 1914. An aneroid barometer should not be relied on.

For barometer readings below 640 mm the correction can be interpolated, since the difference, at any particular temperature, for each 10 mm variation in barometer reading is practically constant.

WASHINGTON, October 27, 1919.

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BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

No. 98

[August 24, 1920]

RECOMMENDED SPECIFICATIONS FOR VOLATILE MINERAL SPIRITS FOR THINNING PAINTS

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, JULY 26, 1920; P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; J. W. GINDER, TREASURY DEPARTMENT, SECRETARY.

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, The Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specifications to a large number of representatives of the petroleum industries and the paint and varnish industries, and gave careful consideration to the replies which were received in time.]

CONTENTS

1. GENERAL

These specifications apply only to petroleum distillates, known as mineral spirits.

The oils delivered under these specifications shall be genuine and shall conform to the following requirements:

Appearance.—Shall be clear and free from suspended matter and water;

Color.—Shall be "water white";

Spot Test.—Shall evaporate completely from filter paper;

Flash Point.—Shall be not lower than 30° C (86° F) when tested in a closed cup tester;

Sulphur.—Shall be absent, as determined by the white-lead test;

Distillate below 130° C (266° F) shall not exceed 5 per cent;

Distillate below 230° C (446° F) shall be not less than 97 per cent;

Reaction.—Shall be neutral.

2. DETECTION AND REMOVAL OF SEPARATED WATER

Draw a portion by means of a glass or metal container with a removable stopper or top, or with a "thief," from the lowest part of the container, or by opening the bottom valve of the perfectly level tank car. If water is found to be present, draw it all out, record the quantity, and deduct it from the total volume of liquid delivered.

3. SAMPLING.

The method of sampling given under (*a*) should be used whenever feasible. When method (*a*) is not applicable, method (*b*), (*c*), or (*d*) is to be used, according to the special conditions that obtain.

(*a*) While Loading Tank Car or while Filling Containers for Shipment.—Samples shall be drawn by the purchaser's inspector at the discharge pipe where it enters the receiving vessel or vessels. The composite sample shall be not less than 5 gallons and shall consist of small portions of not more than 1 quart each taken at regular intervals during the entire period of loading or filling.

The composite sample thus obtained shall be thoroughly mixed, and from it three samples of not less than 1 quart each shall be placed in clean, dry glass bottles or tin cans, which must be nearly filled with the sample and securely stoppered with new clean corks or well-fitting covers or caps. These shall be sealed and distinctly labeled by the inspector; one shall be delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(*b*) From Loaded Tank Car or Other Large Vessel.—The composite sample taken shall be not less than 5 gallons and shall consist of numerous small samples of not more than 1 quart each taken from the top, bottom, and intermediate points by means of a metal or glass container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the stopper or top is removed and the

container allowed to fill. The sample thus obtained is handled as in (*a*).

(*c*) Barrels and Drums.—Barrels and drums shall be sampled after gaging contents. Five per cent of the packages in any shipment or delivery shall be represented in the sample. Thoroughly mix the contents of each barrel to be sampled by stirring with a clean rod and withdraw a portion from about the center by means of a "thief" or other sampling device. The composite sample thus obtained shall be not less than 3 quarts, shall consist of equal portions of not less than one-half pint from each package sampled, and shall be handled as in (*a*). Should the inspector suspect adulteration, he shall draw the samples from the suspected packages.

(*d*) Small Containers, Cans, etc., of 10 Gallons or Less.—These should be sampled, while filling, by method (*a*) whenever possible; but in case this is impossible, the composite sample taken shall be not less than 3 quarts. This shall be drawn from at least five packages (from all when fewer), and in no case from less than 2 per cent of the packages. The composite sample thus taken shall be thoroughly mixed and subdivided as in (*a*).

4. LABORATORY EXAMINATION

Samples will, in general, be tested by the following methods; but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specifications.

(*a*) Appearance.—Examine to determine compliance with the specifications.

(*b*) Color.—Fill a 200 mm perfectly flat-bottomed colorimeter tube, graduated in millimeters, to a depth of from 40 to 50 mm with the oil to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter place a No. 1 yellow Lovibond glass and run in the same oil until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the oil in the two tubes. If this difference is 150 mm or more, the oil is "water white."

(*c*) Spot Test.—Place five drops of the oil on clean white filter paper and allow the liquid to evaporate at room temperature, away from direct sunlight. There should be no oily spot left after 30 minutes.

(*d*) Flash Point.—Determine with either the "Tag" or Elliott closed-cup tester. The former is preferred, and directions for its use are to be found in A. S. T. M., standards D–56–19. For methods of determining with the Elliott cup, see Proceedings A. S. T. M., paragraph I, page 414, 1917.

(*e*) Sulphur.—Place 25 g of dry white lead in a small porcelain dish and mix thoroughly with 50 cc of mineral spirits. Cover with a watch glass, place on a steam bath for 2 hours, remove, and observe the color after 18 hours. There should be no appreciable darkening of the white lead. This test must be performed in an atmosphere free from hydrogen sulphide.

(*f*) Distillation.—*Apparatus*.—See Fig. 1.

Condenser.—The type of apparatus adopted by the American Society for Testing Materials for the distillation of paint thinners other than turpentine is preferred. In case this apparatus is not available, use an ordinary straight glass tube condenser, about 22 inches long, with 16 inches in contact with the cooling water. The end of the condenser tube should be fitted with an adapter, or should be bent down to a nearly vertical position, and the tip should be cut off or ground down at an acute angle. The tip should extend a short distance into the receiving cylinder.

Flask.—Comparable results can be obtained only by using flasks of the same dimensions. The distilling flask used shall be the standard Engler flask, as used for petroleum distillation, having the following dimensions: Diameter of bulb, 6.5 cm; cylindrical neck, 15 cm long, 1.6 cm internal diameter; side or vapor tube, 10 cm long, 0.6 cm external diameter, attached to neck at an angle of 75°, so that when the flask contains its charge of 100 cc of oil, the surface of the liquid shall be 9 cm below the bottom of the junction of the side tube and neck.

Support of Flask.—Support the flask on a plate of asbestos 20 cm in diameter, having an opening 4 cm in diameter in its center, and heat with an open flame. Surround the flask and burner with a shield to prevent fluctuation in the temperature of the neck of the flask.

Thermometer.—A thermometer such as the one adopted by the American Society for Testing Materials for distillation of mineral thinners should be used.

Receiving Cylinder.—Collect the distillates in accurately graduated 50 or 100 cc cylinders. The so-called normal or precision cylinder of 50 cc capacity, having an internal diameter of 1.5 cm and graduated in 0.2 cc, is preferred. If a cylinder with larger

inside diameter is used, a pasteboard cover should be placed over the top and surround the condenser tube.

Operation.—Place 100 cc of the spirits and several small pieces of pumice (or glass) in the distilling flask and fit the thermometer so that the top of the mercury bulb is level with the bottom of the side tube. Place the flask in position on the asbestos board and connect with the condenser. Apply the heat cautiously at first, and when distillation begins regulate the heat so that the spirits distil at the rate of not less than 4 nor more than 5 cc per

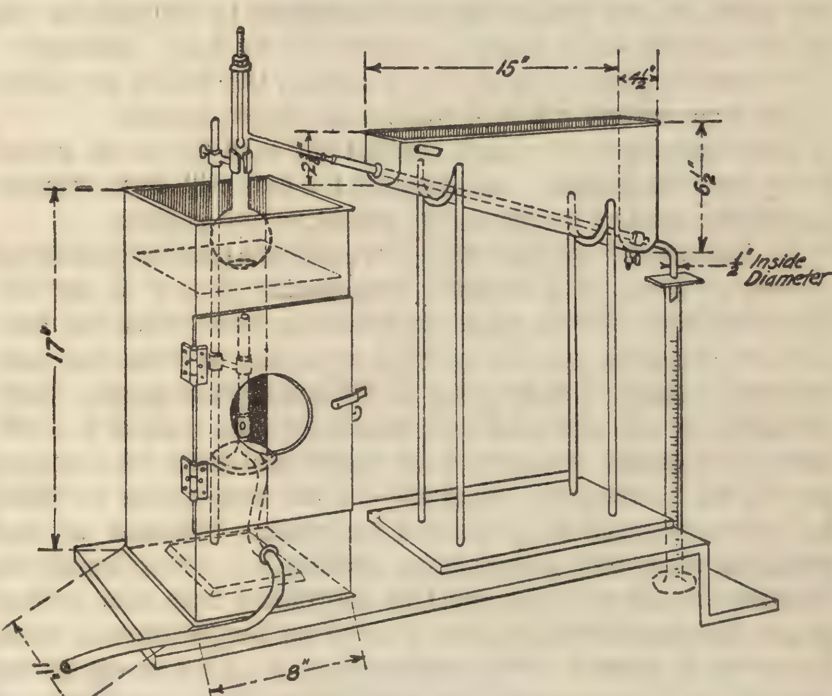

FIG. 1.—*Distillation apparatus*

minute (approximately two drops per second). The initial boiling point is the thermometer reading at the instant when the first drop falls from the end of the condenser. Discontinue distillation when the temperature reaches 230° C (446° F). Let the condenser drain and read the percentage distilled.

The percentage distilled below successive selected temperatures and the temperature at which each successive 10 cc distils may also be determined if desired.

(*g*) REACTION.—Shake 50 cc of the mineral spirits and 50 cc of water in a half-filled stoppered cylinder for one minute, allow to

settle, draw off 25 cc of the water with a pipette, add several drops of phenolphthalein solution and one drop of $\frac{N}{10}$ alkali, which should give the water an alkaline reaction.

5. BASIS OF PURCHASE

(*a*) Unit.—Mineral spirits shall be purchased either (1) by volume, the unit being a gallon of 231 cubic inches at 15.5° C (60° F), or (2) by weight. A gallon of mineral spirits at 15.5° C (60° F) weighs 6.3 to 6.8 pounds. The exact weight in pounds per gallon of any sample can be determined by multiplying the specific gravity at 15.5/15.5° C (60/60° F) by 8.33. Example—If the specific gravity at 15.5° C is 0.7642, the weight per gallon at this temperature will be $0.7642 \times 8.33 = 6.366$ pounds.

When purchased by weight, quotations shall be by the pound or by the 100 pounds. The request for bids will state whether quotations shall be by the gallon, pound, or 100 pounds.

(*b*) Correction of Volume.—The gallonage paid for shall be the volume corrected to a standard temperature of 15.5° C (60° F). The correction shall be made by deducting from (when the temperature of gaging is above 15.5° C) or adding to (when the temperature of gaging is below 15.5° C) the gallonage as gaged. Such deduction or addition shall be computed on the basis of a coefficient of expansion of 0.000945 per degree centigrade (or 0.000525 per degree Fahrenheit). Example—If the temperature at which the spirits is gaged is 75° F, and the volume delivered (at that temperature) is 8000 gallons, then $0.000525 \times 15 \times 8000$ equals the quantity in gallons which must be subtracted from 8000 gallons to give the true gallonage at 60° F, or, if the temperature at which the spirits is gaged is 10° C, then $0.000945 \times 5.5 \times 8000$ equals the quantity in gallons which must be added to the gaged volume of 8000 gallons to give the true gallonage at 15.5° C.

(*c*) Certification.—Mineral spirits delivered in barrels, drums, or tank cars shall either be accompanied by an official gager's certificate showing the net contents of each container and also the temperature of contents at the time of gaging, or shall be subject to gaging by the purchaser's inspector. In the absence of a statement of the temperature at the time of gaging on the official gager's certificate, or in case the barrels show evidence of loss by leakage or other shortage, the delivery shall be subject to reinspection and regaging by the purchaser's inspector.

Washington, July 26, 1920.

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DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

No. 102.

OCTOBER 18, 1920

RECOMMENDED SPECIFICATION FOR COMPOSITE THINNER FOR THINNING SEMIPASTE PAINTS WHEN THE USE OF STRAIGHT LINSEED OIL IS NOT JUSTIFIED

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, SEPTEMBER 27, 1920; P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; J. W. GINDER, TREASURY DEPARTMENT, SECRETARY

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specification to a large number of representatives of the paint and varnish manufacturers, and gave careful consideration to the replies received.]

CONTENTS

1. GENERAL

This specification covers a composite thinner which contains in one liquid drying oil, drier, and volatile thinner. Such preparations are sometimes called "Thinning Mixtures for Paint," and are also offered under a variety of trade names, such as "Japan Oil," "Paint Oil," "Linseed Oil Substitute," etc. The last name should, however, not be used, for while such materials may have decided merit they are not substitutes for linseed oil.

The composite thinner must meet the following requirements:

APPEARANCE.—Shall be clear and free from suspended matter and sediment.

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COLOR.—No darker than a solution of 6 g of potassium dichromate in 100 cc pure sulphuric acid of specific gravity 1.84.

ODOR.—Not offensive, either in bulk or in its subsequent use in paint mixtures.

MIXING WITH LINSEED OIL.—When mixed in any proportion with pure raw linseed oil meeting the specifications of B. S. Circular 82, the resulting mixture shall be clear and shall show no separation or precipitation on standing 18 hours.

DRYING.—When flowed on glass, the composite thinner shall set to touch in not more than 4 hours and dry hard in not more than 6 hours. When mixed with an equal volume of pure raw linseed oil, the resulting mixture when flowed on glass shall set to touch in not more than 6 hours and dry hard in not more than 8 hours.

TOUGHNESS.—The film on glass after baking for 6 hours at 105 to 110° C (221 to 230° F) shall be glossy, tough, and elastic.

NONVOLATILE MATTER.—Not less than 50 per cent by weight.

ACID NUMBER.—Not more than 12, calculated to basis of nonvolatile matter.

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole. Whenever possible an original unopened container shall be sent to the laboratory, and when for any reason this is not done, the inspector shall thoroughly mix the contents of the containers sampled, transfer not less than 1 quart to a clean, dry, glass bottle or tin can, which must be nearly filled with the sample, securely stoppered with a new, clean cork or well-fitting cover or cap, sealed, and distinctly labeled by the inspector. The inspector should take a duplicate from the container sampled to hold for check in case of dispute, and when requested should take a sample for the seller.

3. LABORATORY EXAMINATION

Samples will, in general, be tested by the following methods, but the purchaser reserves the right to apply any additional tests or use any available information to ascertain whether the material meets the specification.

(*a*) APPEARANCE.—Fill two test tubes of the same size (15 cm or 6 inches), with the thoroughly mixed sample to within 2.5 cm (1 inch) of the top. Stopper the tubes with clean corks. Let stand for 24 hours. Note whether sediment is evident in

the tubes; if not, shake one tube vigorously and compare the two tubes. If they still look alike and the liquid appears clear, the sample is considered free from sediment and suspended matter.

(*b*) Color.—Prepare a standard color solution by dissolving 6 g of pure powdered potassium dichromate in 100 cc of pure concentrated sulphuric acid of specific gravity 1.84. Gentle heat may be used if necessary to perfect the solution of the dichromate. The standard color solution and a sample of composite thinner to be tested shall be placed in clear, thin-walled glass tubes of the same diameter. The color comparison shall be made by placing the tubes close together and looking through them by transmitted light. The tubes used for this test should be 1.5 to 2.0 cm (5/8 to 13/16 inch) in diameter and shall be filled to a depth of at least 2.5 cm (1 inch).

(Since the potassium dichromate-sulphuric acid must be freshly made for this color comparison, it is frequently more convenient to compare samples with a permanently sealed tube of composite thinner which has previously been found to be slightly lighter in color than the standard solution of 6 g dichromate in sulphuric acid. When samples are found to be darker than this sealed tube of composite thinner, the dichromate standard should be made up for final decision.)

(*c*) Odor.—Note the odor of the material in bulk, pour a small portion in a shallow flat-bottomed dish, and allow to stand exposed to the air for not less than 48 hours. Flow some on a glass plate and allow to dry in a vertical position for not less than 48 hours. Note the odor of these test portions from time to time. A mild odor of wood turpentine or of fish oil should not be cause for rejection, but a pronounced offensive odor, either due to very crude wood turpentine, rank fish oil, or other offensive substances, would be cause for rejection.

(*d*) Mixing with Linseed Oil.—Thoroughly mix 25 cc of the sample with 25 cc pure raw linseed oil and transfer portions of the mixture to two similar test tubes which shall be filled to within 2.5 cm (1 inch) of the top and stoppered with clean corks.

Thoroughly mix 5 cc of the sample with 45 cc of pure raw linseed oil and transfer portions of the mixture to two similar test tubes which shall be filled to within 2.5 cm (1 inch) of the top and stoppered with clean corks.

Let the four tubes stand for 24 hours and note if any sediment or curdling is apparent in any of the tubes. If not, shake one tube

of each pair vigorously and then compare with the unshaken tube of the same dilution. If the tubes of the same dilution still look alike, the sample is considered to mix properly with linseed oil.

(*e*) Drying.—Pour the undiluted sample and the mixture with an equal volume of linseed oil on clean glass plates not less than 15 cm (6 inches) long and 10 cm (4 inches) wide. Place the plates in a nearly vertical position in a well-ventilated room but not in the direct rays of the sun. The temperature of the room should be from 21 to 32° C (70 to 90° F). The films are tested at points not less than 2.5 cm (1 inch) from the edges of the films by touching with the finger. The material is considered to have set to touch when gentle pressure of the finger shows a tacky condition but none of the material adheres to the finger. The material is considered to have dried hard when the pressure that can be exerted between the thumb and finger does not move the film nor leave a mark that remains noticeable after the spot is lightly polished.

(*f*) Toughness.—Pour the undiluted sample on a clean glass plate. Let drain in a vertical position for 2 minutes, then place in a horizontal position, film up, and let stand at room temperature for 2 hours. Then bake at a temperature of 105 to 110° C
6 (221 to 230° F) for 6 hours. Remove from the oven and let stand at room temperature for not less than 18 hours. The resulting film shall be glossy and when tested with a knife blade shall show elastic properties, turning up with the blade of the knife in an elastic ribbon without cracking or breaking. The film shall also stand rapid light rubbing without breaking the surface.

(*g*) Nonvolatile Matter.—Place a portion of the sample in a stoppered bottle or weighing pipette. Weigh the container and sample. Transfer about 1.5 g of the sample to a weighed flat-bottomed metal dish about 8 cm in diameter (a friction-top can plug). Weigh the container again and by difference calculate the exact weight of the portion of sample transferred to the weighed dish. Heat the dish and contents in an oven maintained at 105 to 110° C (221 to 230° F) for 3 hours. Cool and weigh. From the weight of the residue left in the dish and weight of the sample taken calculate the percentage of nonvolatile matter.

(*h*) Acid Number.—Place a portion of the sample in a stoppered bottle or weighing pipette. Weigh the container and sample. Transfer an amount corresponding to between 1 and 2 g of nonvolatile matter (see (*g*)) to a 200 cc Erlenmeyer flask, reweigh the container and calculate the exact weight taken, add

25 cc of neutral pure benzol and 25 cc of neutral ethyl alcohol, or ethyl alcohol denatured with pure benzol or pure methyl alcohol. (The alcohol used in all cases must be neutral.) Boil for 30 minutes. (It is best to use a reflux condenser.) Cool to room temperature, add 4 drops of phenolphthalein indicator solution, and titrate with standard alcoholic sodium hydroxide. From the number of cubic centimeters of standard hydroxide solution calculate the acid number to the basis of the nonvolatile residue. (Acid number is milligrams of KOH required to neutralize acid in 1 g of material tested.)

4. REAGENT

ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. Standardize against half normal sulphuric or hydrochloric acid, using phenolphthalein as indicator. This standardization must be made each day that the solution is used.

This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc) kept at about 50° C for 15 days and then distilled.

WASHINGTON, September 27, 1920.

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DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

S. W. STRATTON, Director

CIRCULAR OF THE BUREAU OF STANDARDS

No. 105

[October 18, 1920]

RECOMMENDED SPECIFICATION FOR LIQUID PAINT DRIER

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, SEPTEMBER 27, 1920; P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; J. W. GINDER, TREASURY DEPARTMENT, SECRETARY.

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specification to a large number of representatives of paint and varnish manufacturers, and gave careful consideration to the replies received.]

CONTENTS

1. GENERAL

This specification applies both to straight oil drier—that is, material free from resins or "gums"—and to Japan drier; that is, material containing varnish "gums."

The drier shall be composed of lead, manganese, or cobalt, or a mixture of any of these elements combined with a suitable fatty oil, with or without resins or "gums," and mineral spirits or turpentine, or a mixture of these solvents. It shall be free from sediment and suspended matter. The drier when flowed on metal and baked for 2 hours at 100° C (212° F) shall leave an elastic film. The flash point shall be not lower than 30° C (85° F) when tested in a closed-cup tester. It shall mix with pure raw linseed oil in the proportion of 1 volume of drier to 19 volumes of oil with-

out curdling, and the resulting mixture when flowed on glass shall dry in not more than 18 hours. When mixed with pure raw linseed oil in the proportion of 1 volume of drier to 8 volumes of oil, the resulting mixture shall be no darker than a solution of 6 g of potassium dichromate in 100 cc of pure sulphuric acid of specific gravity 1.84.

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole. Whenever possible, an original unopened container shall be sent to the laboratory, and when for any reason this is not done, the inspector shall thoroughly mix the contents of the container sampled, transfer not less than 1 quart to a clean, dry glass bottle or tin can which must be nearly filled with the sample, securely stoppered with a new clean cork or well-fitting cover or cap, sealed, and distinctly labeled by the inspector. The inspector should take a duplicate from the container sampled to be held for check in case of dispute, and, when requested, should take a sample for the seller.

3. LABORATORY EXAMINATION

Samples will in general be tested by the following methods, but the purchaser reserves the right to apply any additional tests or use any available information to ascertain whether the material meets the specification.

(*a*) Sediment and Suspended Matter.—Thoroughly mix the sample. Fill two test tubes of the same size (15 cm, or 6 inches) to within 2.5 cm (1 inch) of the top with the sample. Stopper the tubes with clean corks. Let stand for 24 hours. Note whether sediment is evident in the tubes; if not, shake one tube vigorously and compare the two tubes. If they still look alike, the sample is considered free from sediment and suspended matter.

(*b*) Color.—Mix 2 cc drier and 16 cc clear pure raw linseed oil that complies with the specifications of B. S. Circular No. 82. Dissolve 6 g of pure powdered potassium dichromate in 100 cc of pure concentrated sulphuric acid (specific gravity 1.84). Gentle heat may be used if necessary to secure a perfect solution of the dichromate. This solution should be freshly prepared. The color comparison shall be made by placing the 1 : 8 drier-linseed oil mixture and the dichromate-sulphuric acid solution in thin-walled glass tubes of the same diameter, 1.5 to 2 cm (5/8 to 13/16 inch) to depths of at least 2.5 cm (1 inch) and comparing the depth of

color by looking through the tubes across the column of liquid by transmitted light.

(*c*) MIXING WITH LINSEED OIL, SETTING TO TOUCH, AND DRYING.—Mix 1 cc of the sample and 19 cc of clear pure raw linseed oil that complies with the specifications of B. S. Circular No. 82. Thoroughly clean a glass plate, finally washing with benzol and drying. Pour a portion of the mixture of linseed oil and drier over this plate and place the plate in a vertical position in a well-ventilated room, the atmosphere of which is free from products of combustion or laboratory fumes. Allow the remainder of the mixture to stand for 2 hours. No sediment or precipitate should appear. At 1-hour intervals examine the film of oil on the plate by touching it lightly with the finger at points not less than 2.5 cm (1 inch) from the edges. If the film still has the greasy feel of fresh linseed oil, it has not set to touch. If the film feels tacky and adheres to the finger, it is considered to have set to touch. If the finger can be drawn lightly across the film without the oil sticking to the finger or the surface being marred by this treatment, the oil is considered dry. In case the test shows time of setting to touch or drying greater than 8 and 18 hours, respectively, a second test shall be run on a different day and the average of the two tests taken.

(*d*) NATURE OF BAKED FILM.—Thoroughly clean with benzol a piece of bright sheet metal, either bright sheet iron, tin plate, or terneplate. Shake the sample of drier thoroughly and flow enough on the plate so that a space at least 7.5 cm (3 inches) wide is covered. Allow the plate to stand in a vertical position at room temperature for 30 minutes and then hang in an oven at a temperature of 100 to 105° C (212 to 221° F) for 2 hours.

Remove the plate from the oven and allow it to stand at room temperature for not less than 1 hour. Test the film of drier with a knife blade at a point not less than 2.5 cm (1 inch) from the edge. If the film powders or particles fly under the knife blade, it will be considered brittle, which will be cause for rejection.

(*e*) FLASH POINT.—Determine with either the "Tag" or Elliott closed-cup tester. The former is preferred and directions for its use are found in the A. S. T. M. Standards, D 56–19. For the method of determining with the Elliott cup see Proceedings A. S. T. M., 1917, part 1, p. 414.

4. BASIS OF PURCHASE

Drier shall be purchased by volume, the unit being a gallon of 231 cubic inches at 15.5° C (60° F). The volume may be determined by measure or, in case of large deliveries, it may be easier to determine the net weight and specific gravity at 15.5/15.5° C (60/60° F) of the delivery. The weight per gallon in pounds can then be determined by multiplying the specific gravity by 8.33. The net weight in pounds divided by the weight per gallon gives the number of gallons.

WASHINGTON, September 27, 1920.

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